SYNTHESIS AND EVALUATION OF GEOPOLYMER PROPERTIES USING SAGO PITH WASTE ASH

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by

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LIST OF ABBREVIATIONS

ASTM	American Society of Testing and Materials
DTA	Differential Thermal Analysis
TGA	Thermo-gravimetry Analysis
SEM	Scanning Electron Microscopy
FTIR	Fourier transforms infrared spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
XRD	X-ray Diffraction Spectroscopy
QXRD	Quantitative X-ray Diffraction
XRF	X-ray Fluorescence
LOI	Loss of Ignition
OPC	Ordinary Portland Cement
FA	Fly Ash
BA	Bottom Ash
POFA	Palm Oil Fuel Ash
RHA	Rice Husk Ash
SCBA	Sugarcane Bagasse Ash
CBA	Cassava Bagasse Ash
GGBS	Ground Granulated Blast Furnace Slag
GFA	Geopolymer Fly Ash
SPW	Sago Pith Waste
SPWA	Sago Pith Waste Ash

GSPWA	Geopolymer Sago Pith Waste Ash
ICSD	Inorganic Crystal Structure Database
RH	Relative Humidity
NaOH	Sodium Hydroxide
Na_2SiO_3	Sodium Silicate
C-A-S-H	Calcium Aluminosilicate Hydrate
N-A-S-H	Sodium Aluminosilicate Hydrate
PS	poly(sialate)
PSS	poly(sialate-siloxo)
PSDS	poly(sialate-disiloxo)

LIST OF SYMBOLS

<	Less than
>	More than
≤	Less than or equal to
≥	More than or equal to
=	Equal to
°	Degree
°C	Degree Celsius
°F	Degree Fahrenheit
MPa	Mega Pascal
Kg/m^3	Kilogram per meter cube
M	Molar
pH	Potential of hydrogen
rpm	Radians per minutes
Å	Angstrom (1×10^{-10})
h	Hour
L	Liter
cm	Centimeter
cm^3	Centimeter cube
m	Meter
mm	Millimeter
P_{max}	Maximum load applied

wt %	Weight percent
%	Percentage
A	Cross sectional area

SINTESIS DAN PENILAIAN SIFAT-SIFAT GEOPOLIMER MENGGUNAKAN ABU DARI HAMPAS SAGU

ABSTRAK

Hampas sagu (SPW) adalah merupakan sisa pertanian yang dihasilkan dari tisu *Metroxylon Sagu* (Sagu Palma). Tanpa rawatan yang sempurna, hampas sagu akan menjadi bahan buangan yang boleh mengakibatkan pencemaran sungai. Pelbagai kajian telah dijalankan demi memaksimumkan penggunaannya yang secara tidak lansung dapat mengurangkan jumlah sisa yang dihasilkan melalui industri sagu ini. Namun, kajian terhadap penggunaan abu hampas sagu (SPWA) masih kurang jika dibandingkan dengan kajian yang dijalankan terhadap sisa pertanian lain. Oleh itu, kajian terperinci harus dijalankan terhadap penggunaan bahan ini lebih-lebih lagi sebagai bahan alternatif dalam produk geopolimer. Dalam hasil kerja ini, SPWA yang dihasilkan melalui pembakaran dari suhu 500 °C ke 1000 °C untuk mendapatkan suhu optimum akan digunakan sebagai sebahagian bahan gentian (dari 0 ke 40 wt%) untuk menggantikan bahan utama iaitu abu terbang (FA) dalam produk geopolimer. SPWA dan FA akan diproses bersama bahan pemangkin lain seperti natrium hidroksida (NaOH) dan natrium silikat (Na_2SiO_3) dalam penghasilan produk geopolimer. Beberapa kaedah ujian akan digunakan untuk menguji kemampuan SPWA sebagai mekanisma dalam produk geopolymer, antaranya seperti pendarflour sinar-X (XRF), pembelauan sinar-X (XRD), spektroskopi inframerah Fourier-transformasi (FTIR), ujian daya kemampatan, dan mikroskop elektron pengimbasan (FESEM). Berdasarkan hasil kajian, di dapati bahawa komposisi utama di dalam SPWA adalah terdiri daripada CaO dan SiO_2, bersama kehadiran bahan oksida lain seperti MgO, Fe_2O_3, dan Al_2O_3.

Bahan oksida seperti CaO dan SiO_2 adalah merupakan dua bahan penting yang boleh bertindak sebagai bahan pengikat dalam sintesis geopolimer. Kesan penggantian SPWA terhadap FA sebanyak 10% telah meningkatkan kadar kekuatan mampatan sampel geopolimer sebanyak 7% jika dibandingkan dengan hanya menggunakan FA sebagai bahan pengikat. Kekuatan mampatan tertinggi pada 28 hari yang direkodkan adalah melalui sampel yang dirawat dalam suhu panas pada 65 °C (57kN/m^2) diikuti dengan suhu ketuhar pada 70 °C (47kN/m^2) dan suhu bilik pada 28 °C (45kN/m^2). Tambahan pula, berdasarkan perkiraan mudah, jumlah sisa hampas sagu yang dibakar adalah dalam lingkunagn 0.05 ton setiap 1 ton SPW dibakar.

Oleh yang demikian, dengan peggunaan SPWA sebagai bahan alternatif kepada produk geopolimer ini, sisa SPW yang terhasil dari industri sagu ini dapat diselenggara dengan baik dan secara tidak lansung permasalahan berkaitan dengan pencemaran air juga akan dapat dikurangkan.

SYNTHESIS AND EVALUATION OF GEOPOLYMER PROPERTIES USING SAGO PITH WASTE ASH

ABSTRACT

The sago pith waste (SPW) is a fibrous starch generated from pith of *Metroxylon Sagu* (Sago Palm), known as an agricultural waste, dumped into nearby rivers without proper treatment, leading to river pollution. Several studies have been conducted to maximize the potential use of SPW and minimize the amount of waste generated by the sago industries. Yet, there is still lack of investigation on the utilization of SPW ashes (SPWA) compared to other agricultural waste materials. Thus, the study of SPWA as an alternative raw material, especially in geopolymer products fabrications requires further investigations. In this work, the optimum SPWA obtained from calcination temperatures (500 °C to 1000 °C) was used as a partial replacement material (0 to 40 wt. %) in main source material fly ash (FA). These materials are prepared with a combination of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) as an activator in geopolymer product fabrication. The X-ray florescence (XRF), X-ray diffraction (XRD), Fourier transform infrared (FTIR), mechanical compression testing, and field emission scanning electron microscopy (FESEM) were used as a tools to investigate the viability of SPWA underlying the mechanisms of geopolymerisation. This study revealed that the SPWA mainly composed of CaO and SiO_2 with the presence of other oxides such as MgO, Fe_2O_3, and Al_2O_3. CaO and SiO_2 oxides in SPWA are very significant oxides which are beneficially can be used as an alternative binder for the synthesis of geopolymer products. The compressive strength of geopolymer (GSPWA) mortar at 10% of FA replacement has shown 7% increase compared to normal mortar which utilising on FA as a binder. The highest strength at

28 days is recorded by heat-cured at 65 °C (57 kN/m^2) followed with oven-cured at 70 °C (47 kN/m^2) and ambient temperature at 28 °C (45 kN/m^2). Furthermore, by simple calculations it is shown that the amount of SPWA generated via calcination process is around 0.05 tonne for each tonne of SPW material used. Therefore, the significant of utilizing SPWA as a new alternative raw material especially as a geopolymer product fabrications are two-fold; the waste generated from SPW industry can be manage wisely, whilst the water pollution created by SPW industry can also be minimized.

CHAPTER ONE

INTRODUCTION

1.1 Research background

A geopolymer material is one of technological innovations that recognized by the industry as a green and eco-friendly materials. This technology has been introduced since decade and has its own ancient roots where construction building of the pyramids at Giza and other construction buildings were still magnificence and strong until now (Davidovits, 1984; Barsoum et al., 2006; Davidovits, 2008). By definitions, geopolymer is a framework structures produced by condensation of tetrahedral aluminosilicate units, with alkali metal ions balancing the charge associated with tetrahedral Al. It is a synthesis of two mixtures, consisting of an alkaline solution (as activator) and solid aluminosilicate materials. The process of geopolymerization can occurs either at ambient temperature or elevated temperature, where the leaching of solid aluminosilicate raw materials in alkaline solutions leads to the transfer of leached species from the solid surfaces into a growing gel phase, followed by nucleation and condensation of the gel phase to form a solid binder.

Geopolymer was first discovered and introduced by Joseph Davidovits in 1978 by describing a family of mineral binders with chemical compositions similar to zeolites but in amorphous microstructure (Davidovits, 2008). Basically, the sources materials for the formation of geopolymers should rich in silica (SiO_2) and alumina (Al_2O_3), either natural minerals such as kaolinite, clays, micas, andalusite (Davidovits, 2008) or by-product material such as fly ash (FA) (Nazari et al., 2011), silica fume, red mud ash (Jian et al., 2013) and palm oil fuel ash (POFA) (Chandara et al., 2010; Yusuf et al. 2014). Whilst, soluble alkali metals such as sodium or potassium based used to activate the polymerization reaction.

By comparing with ordinary Portland cement (OPC) which are very common for concrete as a construction material, geopolymer material has excellent durability and may exhibit many other useful properties such as high compressive strength, low shrinkage, acid and fire resistance (Hardjito & Rangan, 2005). Furthermore, the production of OPC releases a considerable amount of greenhouse gas because of decarbonation of limestone in the kiln during manufacturing of cement and the combustion of fossil fuels. Besides, Temuujin and Van Riessen (2009) states that, OPC is the most energy intensive construction materials, after aluminium and steel. They also mention that the contribution of carbon dioxide (CO_2) to global warming by the cement industry is well established. Since CO_2 emission is about 0.7–1.1 tonnes per ton of cement produced and about 50% of this attributed to limestone calcination, 40% to fuel combustion in the kiln, and the remaining 10% to manufacturing processes and product transportation. Therefore, the search for an alternative binder or geopolymer materials for the purpose to replace OPC is important effort towards environment sustainability.

Past researchers have published a large number of publications and review papers on geopolymer synthesis and characterization. Initiated by French author Davidovits that developed and patented the binders obtained from the alkali-activation of metakaolin named as geopolymer in 1978 (Basoaga et al., 2009). Geopolymerizations is a complex multiphase exothermic process involving series of dissolution, reorientation and solidification reactions analogous to zeolite synthesis

(Davidovits, 2011; Provis, 2014). Other industrial based aluminosilicate materials such as coal, FA, and natural minerals such as kaolin and calcined clay also used in synergy for the geopolymer synthesis. Currently, a new approach introduced in geopolymer materials utilizing natural agro waste materials, categorized as a pozzolanic material (Cordeiro et al., 2009; Thangavelu et al., 2014). Agro waste products such as POFA (Chandara et al., 2012), rice husk ash (RHA) (Della et al. 2002), sugar cane bagasse ash (SCBA) (Morales et al., 2009), and cassava bagasse ash (CBA) (Sugumaran et al., 2014) are few examples of pozzolanic materials that have been used either as a binary mixes with other aluminosilicate materials such as ground granulated blast furnace slag (GGBS), FA or bottom ash (BA) (Geetha & Ramamurthy, 2013) or as a source material in order to produce geopolymer concrete.

Moreover, these pozzolanic materials, which have reactive silicates or alumino-silicates, chemically react with alkalis and calcium hydroxide to produce cementitious compound has many other beneficial features such as economic saving, green and environmental friendly material, increase durability and workability. POFA is one of the example, which is the most common pozzolans available in countries such as Malaysia, Indonesia and Thailand, resulted in higher compressive strength compared to OPC. This is a major significance impact since the utilization of POFA offer waste utilization and CO_2 emission reduction (Mijarsh et al., 2014). Other than POFA, sago pith waste (SPW) is another new potential agro waste material in South East Asia countries especially in Indonesia, Papua New Guinea and Malaysia which is abundantly burn or mostly dumps into riverside after being extracted (Figure 1.1(c) and Figure 1.1(d)). SPW was produce by extracting sago (Figure 1.1 (a) and Figure 1.1 (b)) particularly *Metroxylon sagu* which is traditionally used as food product. It identified as one of industrial wastage as tonnes of sago biomass such as sago fibers, sago barks and SPW generated every day. This agricultural waste is possibly contained high amount of SiO_2 and calcium carbonate ($CaCO_3$) when SPW burned to specific burning temperatures as sago pith waste ash (SPWA). SiO_2 and $CaCO_3$ are very useful compounds used as pozzolanic material via proper treatment, thus utilize as geopolymer materials. In this context, the present work is the first such effort to explore and quantify the potential of a new alternative material that comes from this agro waste material (SPWA) to substitute other pozzolanic materials for geopolymer product. Therefore, this research considered as a very significance effort to sago related industries and at the same time contributing to environmental sustainability. Consequently, this study should be able to solve the wastewater problem that comes from SPW industry, whilst utilization of SPWA as geopolymer materials could lessen CO_2 emission in the production of OPC.

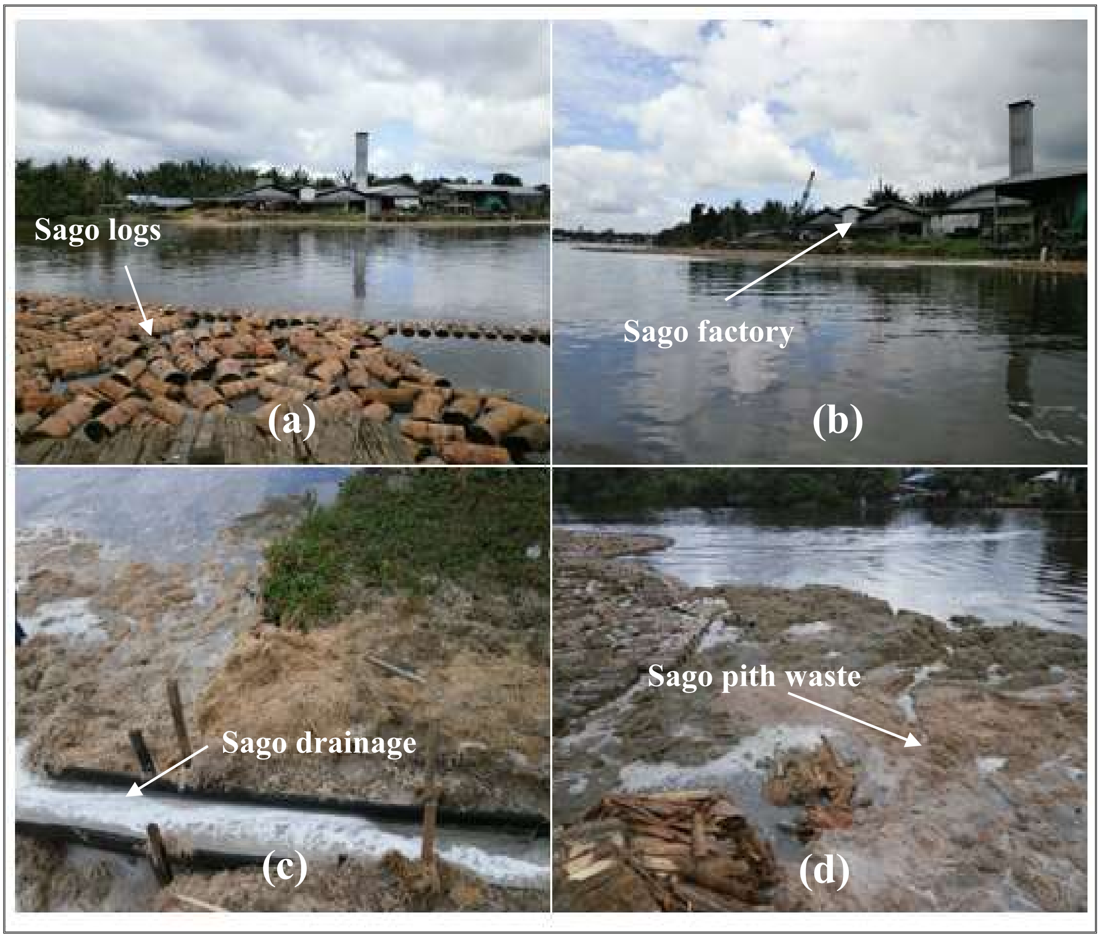


Figure 1.1 Sago extraction factory and effluent of SPW; (a) Sago logs, (b) Sago factory, (c) Sago waste drainage, and (d) Sago pith waste.

1.2 Problem Statement

Sago palm is one of the crops that can grow well in wild, limited natural stands, swampy area and acidic peat soil (Wan et al., 2015). It can be extracted from the spongy center, or pith of various tropical palm stems to obtained sago specifically *Metroxylon sagu* (Lai et al., 2013). Sago, which is traditionally cooked or eaten in various forms, found in tropical lowland forest in South East Asia countries such as in Indonesia, Papua New Guinea and Malaysia. The amounts of sago starch produced by these three countries are approximately 2.4 million hectares of total sago palms. In Malaysia, sago palm can be found in Sarawak, a state in

Northern Borneo, especially in Oya-dalat, Mukah, Pusak-Saratok, Igan and Balingan (Abdul Aziz, 2002). These sago factories are built near riverside area for ease of transportation purposes and waste management. For every tonne of sago starch produced during the extraction process, huge amount of sago biomass such as sago fibres (1.41 tonnes), sago barks (1.73 tonnes), and sago pith wastes (SPW) (> 20 tonnes) are generated without proper treatment (Bujang, 2008; Adeni et al., 2009).

Based on export data of sago starch published by Department of Agriculture Sarawak (2013), it is estimated more than 68,000 tonnes of fibers, 83,000 tonnes of barks, and 960,000 tonnes of wastewater generated annually. The installation of pollution control devices is one of the best methods to solve this problem but these disposal methods could cost about 20 - 50% of the total investment in a large-scale factory (Awg Adeni et al., 2010). This sago waste used as flooring material or burnt off for animal food. These practices can cause more wastage of valuable energy, whilst causing an environmental problem especially related to river and air pollutions. Several studies conducted to resolve the problems and to explore any other potential uses of SPW as to improve the sustainability of sago industry. These include an investigation on cadmium sorption characteristics of phosphorylated sago starch-extraction residue (Igura & Okazaki, 2010), as a probe for metal ion sensing (Tan et al., 2014), as well as its use as craft paper (Wan Mohamad Daud et al., 2010). A study by Quek et al. (1998), on the usage of SPW for the sorption of lead and copper is also one of the efforts to minimize waste from the sago industry. In addition, a study by Kadirvelu et al. (2004), reported that SPW used as an alternative low-cost adsorbent and found that SPW activated carbon was very effective in removing Hg (II) from aqueous solutions and industrial effluents.

However, a systematic investigation on the utilization of SPW ash (SPWA) generated during the conversion of sago fibers and SPW to energy by burning is still lacking compared to investigations done on other agricultural waste materials, such as RHA, SCBA, CBA and POFA. The utilization of these materials with other by-product materials such as FA, BA, and GGBS, which are rich in alumina compound, are very significant to industries. Thus, SPWA that is possibly contained SiO_2 and $CaCO_3$ has this advantage as well as other agricultural waste materials via substitution in the production of geopolymer product. To date, no reports and researches conducted on the utilization of SPWA to make any value-added products. Very similar to other ashes generated from other agricultural wastes, there is a strong possibility that SPWA also used as a new resource of raw material, especially for the fabrication of geopolymer products. Therefore, the focus of this investigation is on the characterization and evaluation of SPW and SPWA used as a new resource of raw material, especially for the fabrication of geopolymer products.

1.3 Research Objectives

The research objectives of the study are as follows:

i. To characterize and analyze the potential of SPW and SPWAs as a new pozzolanic raw material.

ii. To optimize the usage of SPWA to partially replaced FA (main source) in geopolymer product fabrication.

iii. To evaluate the performance of optimized SPWA-based geopolymer products.

1.4 Research scope

The main important components of geopolymer mortar are mixtures of solid material and alkaline activator. The solid materials used in this study is FA (as main source material) partially replaced with SPWA. The alkaline activator is prepared using NaOH and Na_2SiO_3. All of the material components for geopolymer mortar were obtained locally such as SPW, which was collected from River Link Sago Resources Sdn. Bhd. Mukah, Sarawak, Malaysia whilst Raw FA was collected from Stesen Janaelektrik Sultan Salahuddin Abdul Aziz, Kapar, Selangor, Malaysia.

CHAPTER TWO

LITERATURE REVIEW

2.1 Sago as a sources of food

Sago or starch containing palm pith, also scientifically known as *Metroxylon sagu*, comes from genus *metroxylon* and family palmae (Singhal et al., 2008). It is originally Javanese, which means starch containing palm pith is considered as the 'starch crop of the 21st century' by many scientists (Jong, 1995). Sago palm is an economical and environmental friendly crops that promotes a socially stable agroforestry system (Flach, 1997). The palm is an extremely hardy plant, commonly can be found in tropical lowland forests, acidic peat soils, and submerged in freshwater swamps and salty soils. It can immune to floods, drought, fire and strong winds. The large fibrous root system traps silt loads and removes pollutants, faecal contaminants and heavy metals (Flach & Schuilling, 1989; Jong, 1995).

In many countries, sago is traditionally cooked and eaten in various forms (Figure 2.1). It is also has been used in some industries producing noodles, biscuits, chips, bread and has potential to be used as thickener in the production of soup and baby food, as well as an additive in various food products (Karim et al., 2008). Production of sago (2 to 3 tonnes starch/ha/year) is higher compared to other crops such as cassava (2 tonnes) and maize (1 tonne) (Stanton, 1993). The sago industry is well-known being dominated by three leading world producers which are Malaysia, Indonesia, and Papua New Guinea. Here, sago is grown commercially and around 2.4 million hectares of total sago palms is planted for the production of sago starch and/or conversion to animal food or ethanol (Hisajima, 1994).

Figure 2.1 Types of sago food product

In Malaysia, the largest sago forest can be found in Sarawak especially in Oya-dalat, Mukah, Pusak-Saratok, Igan and Balingan (Abdul Aziz, 2002). Sarawak is known has the highest productivity among the starchy crops of the world, exporting annually about 25,000 to 40,000 tonnes of sago products to Peninsular Malaysia, Japan, Taiwan, Singapore, and other countries (Ishizaki, 1997). However, the consequences from this industry was something else. It was estimated that 600 logs of sago palm were cut per day, 15.6 tonnes of woody bark, 237.6 tonnes of waste water, and 7.1 tonnes of starch fibrous sago pith residue are generated (Bujang & Ahmad, 1999). This residue is identified as one of an industrial wastage, since they are continuously generated every day without treatment before being dumped into nearest riverside.

2.2 Sago pith waste (SPW)

Sago pith residue which also known as SPW, is formed from the extraction process after most of the starch has been extracted from the rasped pith of the sago palm (Singhal et al. 2008). Most of the SPW contains 60 to 80 wt% of sago starch grains trapped within the lignocellulosic fibre matrix (Chew & Shim, 1993). Approximately one tonne of SPW were generated from every tonne of sago starch produced. It is either left in the surrounding of sago mill as flooring material or burnt off for animal food. This wastage is also found to produce unpleasant smell, distraction scenery and most of all as major sources of river pollution. Since some of larger manufactures was not utilised SPW properly and washed off this residue into the waterways together with the wastewater (Cecil, 1982).

Sriroth (1999) reported that this waste is difficult to manage as it cannot easily dried, due to its high moisture and starch contents. Thus, it becomes an environmental nuisance and source of pollution. Mohd et al. (2001) estimated the amount of starch disposed as SPW in the state of Sarawak alone accounted for nearly half of the total Malaysian annual imports of starch (40,000 tonnes). Moreover, water quality drops severely and further endangers the aquatic lives because the microbiological degradation of the waste consumes oxygen dissolved in the water, leaving the water with insufficient oxygen to support higher forms of life (Cecil, 2002).

2.2.1 Properties of SPW

According to Chew and Shim (1993), SPW contains a large number (60 – 80 wt%) of sago starch granules which are trapped within the lignocellulosic fibre matrix. Whilst Linggang et al. (2015), found that the content in SPW is mostly consist of starch, with other small part of fibre such as cellulose, hemicellulose, and lignin. This is shown that SPW has a unique characteristic compared to other starch-containing fibrous wastes such as cassava bagasse. It is very potential to be used as biodegradable composite material without adding any synthetic plastic as binder via different processing techniques such as compression moulding, injection moulding and thermoforming (Lai et al., 2013). Furthermore, Lai et al. (2013) found that SPW which is a mixture of sago starch and SPW fibres is an interesting candidate for producing biodegradable composites. The utilization of this waste offers another significant alternative solution towards sustainability by mitigating the effluent of water-polluting waste and even providing an extra incentive to sago starch extraction plant.

2.2.2 Applications of SPW

Generally, SPW is a well-known waste material that can be used as an animal feed or can be compost for any vegetable natural fertilizer. It is also can be used as compost for mushroom culture, and substrate for local microbes to produce reducing sugars and enzyme (Vikineswary et al., 1994). Despite of having tonnes of valuable raw material wastage and water quality contamination due to the process of discharging SPW into river, researchers also has played an important role in order to minimise the waste generated and maximise the usage of SPW as a new raw material product by conducting several studies. Wan Mohamad Daud et al. (2010) is one of the researchers that utilising SPW by converting the waste material into art paper. The effort was a successfully significant as they found that the bleached sago kraft paper provide a white stable surface for watercolour painting whilst SPW can be used as cardboard type product for making gift boxes of various designs with uniform consistency and rigidity.

A study by Quek et al. (1998), on the usage of SPW for the sorption of lead and copper is also one of the efforts that have been done to minimize waste from the sago industry. The study found that sago waste is a better adsorbent for lead than for copper, having the higher initial sorption rate and the greater sorption capacity. Besides, a study by Kadirvelu et al. (2004), reported that SPW could be utilized as an alternative low-cost adsorbent and found that SPW activated carbon was very effective in removing Hg (II) from aqueous solutions and industrial effluents. Another interesting study conducted by Zainab et al. (2013) was utilizing SPW as a fire retardant sound-absorbing panels for the music industry. The function and basic manufacturing of the panels were similar to other products available in the market. But this panel showed an excellent anti-termite property, fire resistant and its do not require any high technology for the mass production and commercialisation.

Furthermore, other than being used directly as value added product, SPW which is a starchy lignocellulosic by-product (Singhal et al., 2008) also can be used as a source of renewable energy for bioethanol production. This production which mainly produced from sugar containing and starch grains (Thangavelu et al., 2014) has been changed using lignocellulosic biomass due to its feed value (Balat et al., 2008). SPW which categorized as biomass and bioenergy crops is one of the potential main sources for economic bioethanol production (Limayem & Ricke, 2012) similar to other starchy lignocellulosic biomass such as waste from starch processing factories, potato food factories, beverage, and brewery factories (Kosugi et al., 2009; Su et al., 2010 and Oberoi et al., 2011). Moreover, study by Maizirwan et al. (2010), has also found another significant finding to maximize the usage of agricultural waste such as SPW as the production of biogas energy. The study are purposely to introduce a potential biogas production from agricultural wastes such as SPW that can be used as fuel through anaerobic digestion. Highlighting the important usage of biogas which can reduce the adverse impact on the environment, can be cleaned and upgraded to biomethane, a gas indistinguishable from conventional natural gas that can be used as a fuel.

However, as SPW being utilize for renewable sources of energy, another possible problem arose. SPW ash (SPWA) will be generated during the burning process. The valuable compounds in this ash that is possibly present as in most of agro waste materials are SiO_2 and $CaCO_3$. But, it is improperly managed and remains as a waste. With this regard, further exploitation on this waste is required by imitating few other agro waste materials that has been used as a geopolymer product. Since SPWA has almost similar characteristic and categorized as pozzolanic materials. By utilizing SPWA as a geopolymer product, the waste generated by SPW industry can be manage wisely, while at the same time the environmental problem such as CO_2 emission from cement production can be partially solved.

2.3 Geopolymer development

Geopolymer is an innovative technology recognized by the related industry as a green and eco-friendly materials. It is significantly stronger than other cements, impermeable to water, and much more durable to erosion caused by temperature change or chemical action. It can be synthesized from various aluminosilicate sources such as zeolites, kaolinite, metakaolin, calcium, silica, fly-ash, blast furnace slag, and organic minerals. Application of geopolymer has diverse range of potential applications such as in structural and non-structural element, fire and heat coatings and adhesives, high-temperature ceramics, binder as construction application, aeroplanes, shipbuilding, racing cars, and the nuclear power industry (Komnitsas & Zaharaki, 2007). The geopolymer technology has been introduced since decades and has its own ancient roots where construction building of the pyramids at Giza and other construction buildings were still magnificence and strong until now (Davidovits, 1984; Barsoum et al., 2006). This unique technology which is strong and high durability has attract Ukrainian scientist, Victor Glukhovsky attention to further investigated a new superior cement named ‘soil cements’, produced by mixing alkaline based material such as sodium and potassium which are exist in many natural minerals.

This finding was continues with another similar discovery made by Joseph Davidovits, a French chemical engineer who has discovered a new class of materials known as geopolymers. He define the geopolymer as a material originated by inorganic poly-condensation, i.e. by so-called “geo-polymerization”, and geopolymer act as a chains or networks of mineral molecules linked with covalent bond. Whilst Tavor et al. (2007) define geopolymer materials as an amorphous inorganic polymer formed through the ionic bonding reaction between an aluminosilicate (Al-Si) material and a strong alkaline solution. Yet, this definition and terminology are differs and sometimes often conflicting based on the researchers with different background of specialities such as "soil silicate concrete", "soil cement", "alkali-activated cement", "inorganic cement" etc. (Sofi et al., 2007; Palomo et al., 2008).

2.3.1 Geopolymer as an alternative solution for Portland cement

Portland cement is the most preferable and well-known materials used in the industries related to transportation, infrastructure, construction and offshore applications. The production of conventional Portland cement known as Ordinary Portland cement (OPC) was developed since early 19th century. OPC is highly versatile binder, easy to produce and economically viable binder with an estimated worldwide production of around 3 gigatonnes (Juenger et al., 2011). However, the environmental issues through the utilization of OPC are also prominent. Enormous amount of CO_2 emission is released into the atmosphere during the production of OPC which can be the major contributor to the greenhouse effect and reflect the impact of global warming. Thus, the existence of geopolymer materials is the best possible alternative solution for solving environmental problem created by OPC. It can offer wide range of environmental friendly applications, due to its unique properties and characteristic.

Davidovits (1994) reported that more than 65% of the crust of the earth consists of Al-Si which can be used and convert to cement without producing large quantities of CO_2. Moreover, by replacing the usage of OPC with geopolymer materials, another environmental issues can be solved. Unused industrial by-product waste material and natural raw materials which are rich in aluminosilicate such as FA, BA, POFA, and RHA can be recycled through synthesized with alkaline materials in the production of geopolymer materials. To do this, basic understanding on the concept and mechanism of geopolymerisation must be appreciate first. Thus, the main purpose of mitigating environmental issues related to OPC can be done, whilst at the same time good geopolymer material utilizing another waste materials can be produced.

2.3.2 Concept of Geopolymerisation

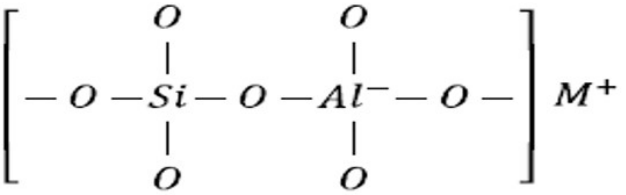
Geopolymer is generically used to describe an amorphous alkali aluminosilicate materials which is also referred as “inorganic polymers”, “alkali activated cements”, “geocements”, etc. These terms all are describe materials synthesized utilising the same chemistry processes (Duxson et al., 2007). It’s consisting of a repeating units of sialate monomer (Si-O-Al-O-). Most of the aluminosilicates materials used in geopolymerizations technology are kaolinite, feldspar and industrial solid residues such as fly ash, metallurgical slag and mining waste. The reactivity of each aluminosilicates sources is differ, depending to its chemical make-up, mineralogical compositions, morphology, fineness and glassy phase content. Another main criterion for developing stable geopolymer are the alkaline activators such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate (Na_2SiO_3) and potassium silicate (K_2SiO_3) which is used to activate aluminosilicate materials. Most of these alkaline activators used, NaOH is a notable activator which can possesses greater capacity to liberate silicate and aluminate monomers (Duxson et al., 2007).

Study by Ikeda (1998) also stated that the synthesis of geopolymers requires three types of sources materials which are raw materials, inactive filler and geopolymer liquor. Raw materials could be natural (alumino-silicate) minerals or industrial wastes such as fly ash, slag, and waste glass. Inactive filler, mainly kaolinite or metakaolinite is used for the supply of Al^{3+} ions. Geopolymer liquor is an alkali hydroxide solution required for the dissolution of raw materials while sodium (or potassium) silicate solution acts as binder, alkali activator and dispersant or plasticiser (Phair, 2001). When alumino-silicate powder is mixed with the alkaline solution a paste forms and quickly transforms into a hard geopolymer. There is no sufficient time and space for the gel or paste to grow into a well crystallised structure; this is the fundamental difference between zeolites and geopolymers. After shorter setting and hardening time, geopolymers with tightly packed polycrystalline structure are formed exhibiting better mechanical properties than zeolites which have lower density and cage-like crystalline structure (Xu and Van Deventer, 2000). These process involves leaching, diffusion, condensation and hardening steps, while on the other hand zeolite synthesis is related to prenucleation, nucleation and crystal growth. In addition, geopolymers usually set at temperatures lower than those required for zeolite manufacture (Davidovits, 1991).

2.3.3 Mechanism of geopolymerisation

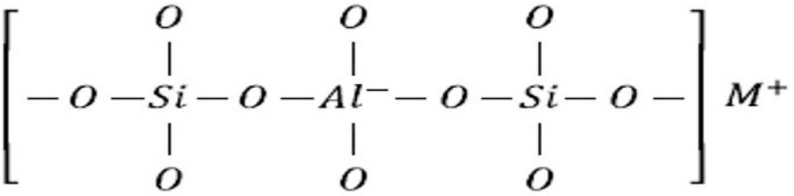
The mechanism for the formation of geopolymer proposed by Davidovits (1994), is categorized into two stages which are chemical reaction of geopolymeric precursors (like aluminosilicate oxides with alkali silicate forming monomers - orthosialate ions) and the exothermal polycondensation of monomers. He set a logical scientific terminology based on different chemical units, essentially for silicate and aluminosilicate materials according to the Si: Al atomic ratio. The basic monomer unit is a sialate, with $M_n(-(SiO_2)_z\text{-}AlO_2)_n.wH_2O$ to be the empirical formula for polysialates, where z is 1,2,3; M is a monovalent cation, such as potassium or sodium;

and n is the degree of polycondensation (Davidovits, 1991). The sialate is a basic monomer stands for the silicon-oxo-aluminate building unit. It is consisting of $[SiO_4]$ and $[AlO_4]^-$ tetrahedral linked alternately by sharing oxygen atoms. The replacement of Al^{3+} (four-fold coordination) with Si^{4+} causes a negative charge, which needs alkalis or alkali earth to balance such as Na^+, K^+, Ca^{2+}or Mg^{2+}. Based on the number of silicon atoms replaced by aluminium, three different types of monomeric -Si-O-Al- structure are believed to define geopolymers. Davidovits (1999) classified the polymeric forms of -Si-O-Al- into poly(sialate)(PS), poly(sialate-siloxo)(PSS), and poly(sialate-disiloxo)(PSDS). The types of polysialates distinguished are illustrated in Figure 2.2 (Davidovits, 1988).



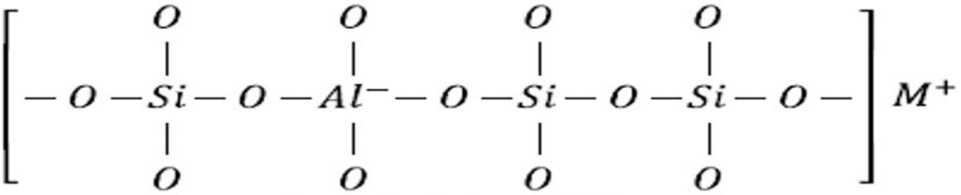
$$\left[-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Al^-}}-O-\right]M^+$$

(poly-) sialate



$$\left[-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Al^-}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O-\right]M^+$$

(poly-) sialate siloxo



$$\left[-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Al^-}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O-\right]M^+$$

(poly-) sialate disiloxo

Figure 2.2 Types of polysialates structural units (Davidovits, 1988)

Structure of the polymeric Si-Al materials formed depends on the ratio of Si/Al in the starting materials and can be classified according to the ratio described by Duxson et al. (2007). More quantity of silicate is required to form the high order structure of PSS and PSDS. Additional Si/Al ratio is achieved with the addition of extra reactive silica using Na_2SiO_3 or silica fume to obtain the precursors. These polymeric precursors make a network which is in the form of ring/chains combined with Si-O-Al bridges in 4-fold coordination with oxygen. K^+ and Na^+ helps in the formation of the geopolymer. The charges of Al atoms are neutralized in order to obtain a stable structure. Conceptual model of potassium-based alumino-silicate geopolymerizationis shown in Figure 2.3. The structure of geopolymer can be either amorphous or crystalline, depending on the condensation temperature. Amorphous polymers are obtained at temperature ranging from 20 to 90 °C, while crystalline polymers are obtained at 150 to 200 °C. PS and PSS can be easily synthesised using sol-gel chemistry at room temperature, and their ranges of applications extend to the immobilisation of toxic waste and construction products. However, PSDS possesses superior physical and thermal properties compared to the formers, thus it can be used as a refractory lining or tooling composite material (Davidovits, 1991).

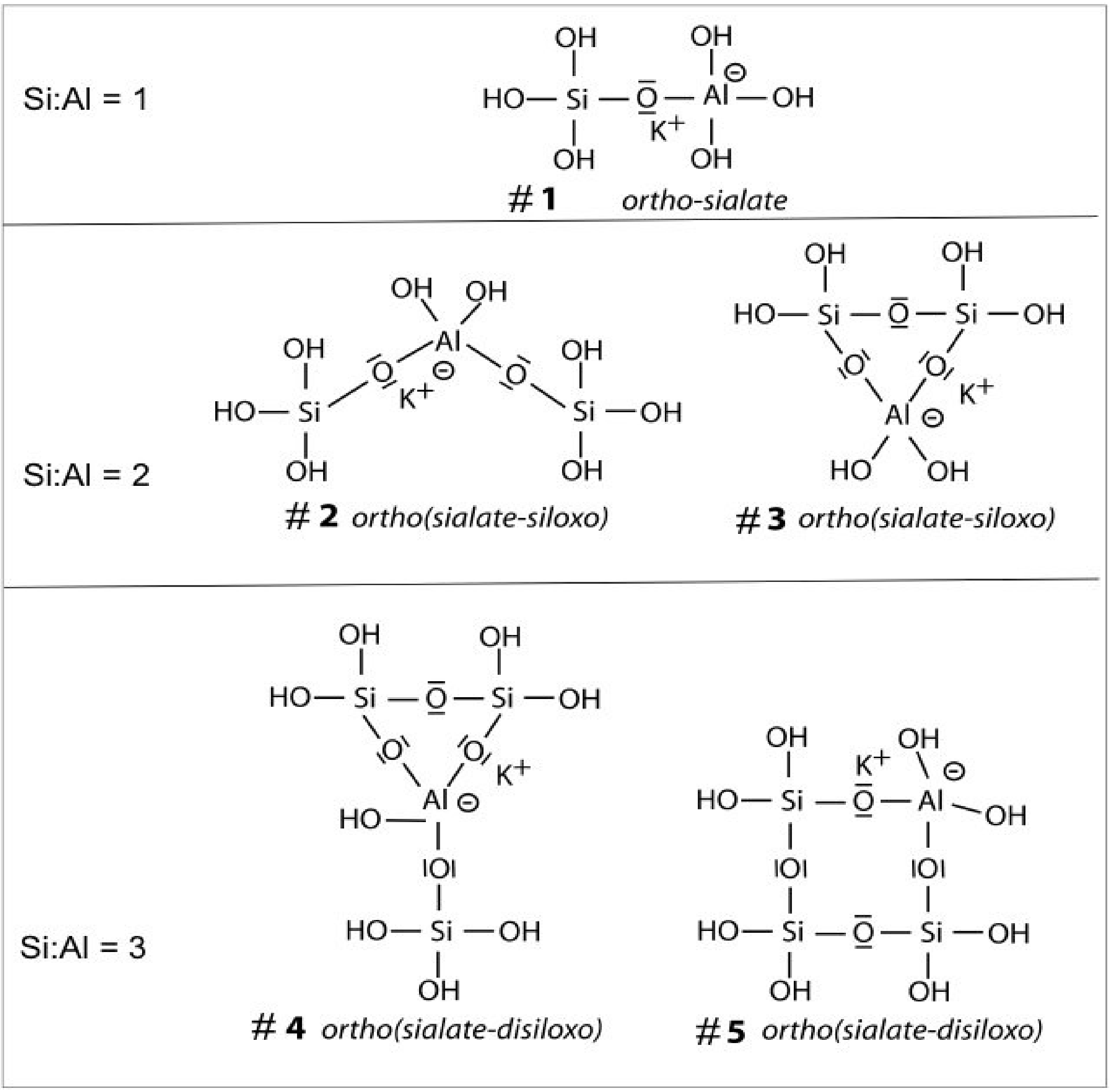


Figure 2.3 Conceptual model of potassium-based alumino-silicate geopolymerizationis (Davidovits, 1988)

Davidovits (1991; 1999) proposed that the macro-molecular structures of PS, PSDS resemble those large, cage structures of zeolites based on the similar mechanism and kinetics observed between the hydrothermal synthesis of zeolites and geopolymers from kaolinite. Na-PS (sodium polysialate) resembles the hydroxysodalite framework of Naphillipsite, K-PS and Ca-PS resemble the frameworks of kalsilite and analcime respectively, while (Na,K)-PSS (sodium, potassium polysialatesiloxo) gives the phillipsite-like framework.

Barbosa and Mackenzie (2003) subjected metakaolinite-based geopolymers (Na- and KPSS structures) to various thermal analyses and observed that there is an initial water loss at around 200 ºC, which is associated with the evaporation of physically-bound water. The water loss at around 200 ºC leads to a small degree of shrinkage; however, the structure of Na-PSS is dimensionally stable at 250-800 ºC. Irreversible shrinkage only occurs at 800 ºC and higher, i.e. when the gel crystallises. The Na-PSS begins to melt at temperatures ranging from 1200-1300 ºC, while the K-PSS shows little sign of melting at 1400 ºC. In this instance, it seems that the K-PSS structure has more thermal stability than Na-PSS, and the thermal properties of both geopolymers are affected by the amount of water in the structure as well. At 1000 ºC, the amorphous structure of KPSS is replaced by the crystalline feldspars, leucite, and kalsilite. An NMR study on both systems suggest that charge-balancing alkali cations in the K-PSS and K-PSDS behave similarly to those in Na-PSS and Na-PSDS respectively, i.e. in terms of dehydration and crystalline transformation mechanisms. On the other hand, Rahier et al. (1996b) has found that the glass transition of metakaolinite-based geopolymers occurs at 650 ºC, rather than at 800 ºC. The difference is mainly caused by the different composition of Si: Al and water content from the geopolymers. In fact, these two factors and also the alkali concentration (Al/M ratio), are parameters that determine the structure and physio-chemical properties of geopolymers.

Barbosa et al. (2000) found that irrespective of composition, curing, and drying method, all types of geopolymers possess a lack of long-range atomic order. This is reflected by the absence of a crystalline XRD pattern and the broad 29Si NMR resonance. The optimum formation of Na-PSS polymer occurs when the ratio of SiO_2/M_2O is 4.0 and the ratio of H_2O/Na_2O is 10. Based on solid-state NMR-MAS study, Barbosa et al. (2000) also proposed a new model for the molecular structure of geopolymer gel, whereby the framework structures are saturated in Al, e.g. SiQ4 (3Al), as shown in Figure 2.4 (SiQ4 (3Al) means there are 3 neighbouring Al atoms for a tetrahedral Si). The new model contains Si and Al tetrahedra which are randomly cross-linked to provide cavities, in order to accommodate the charge-balancing hydrated sodium ions. This arrangement fits with the 29Si and 27Al NMR data as the Q4 (2Al) and Q4 (3Al) are believed to be the two predominant species in metakaolinite-based geopolymers. This model is preferred because its structure is in a more disordered state and possesses the ability to accommodate hydrated sodium ions, unlike the previous models suggested by Davidovits (1991), as shown in Figure 2.5.

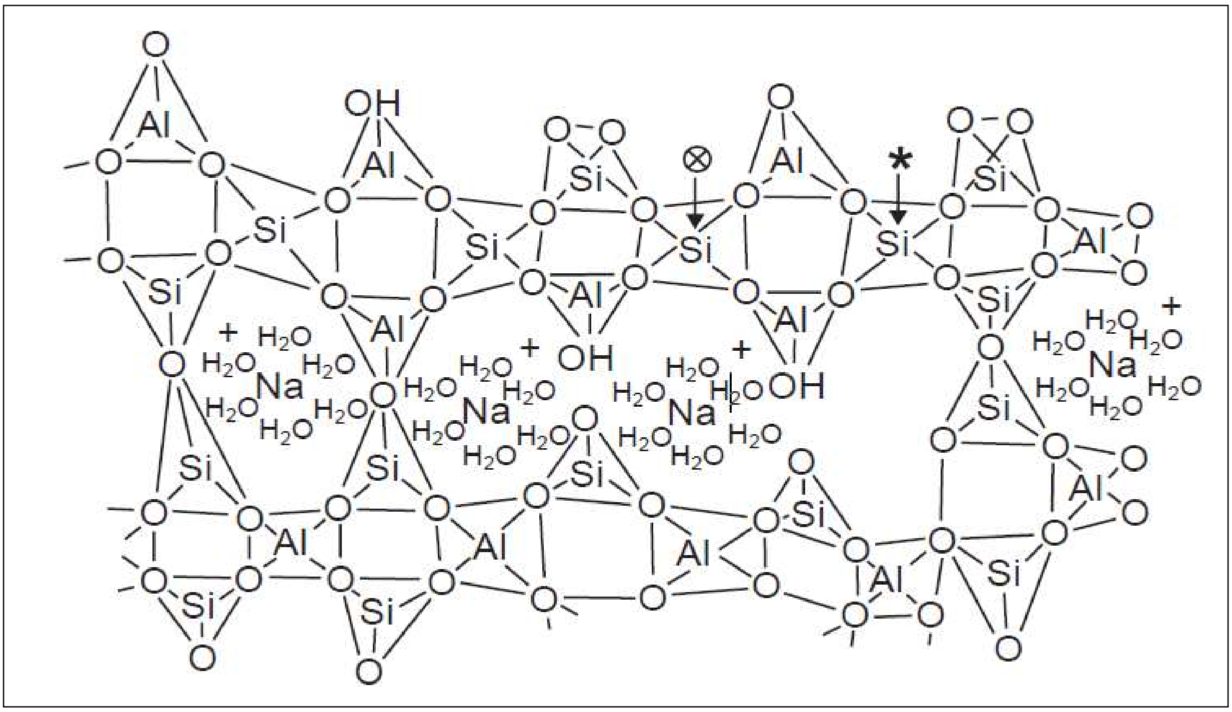


Figure 2.4 Modified model of geopolymer structure (Barbosa et al., 2000)

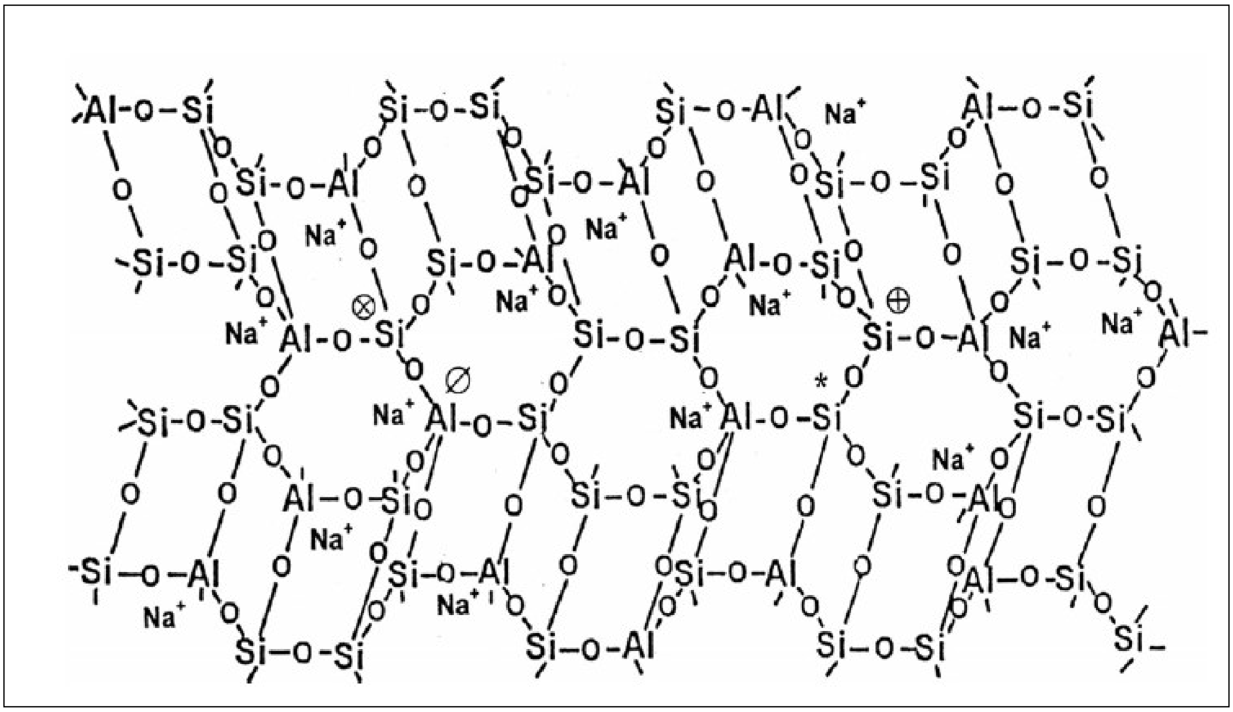


Figure 2.5 Structural model of geopolymer (Davidovits, 1999; Davidovits, 2005)