STUDY OF FLY ASH [illegible] GEOPOLYMER MORTAR: CITRIC ACID AND SUCROSE AS PROPOSED NATURAL BASED RETARDER

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ABSTRACT

The geopolymer then has been introduced by Joseph Davidovits as a new binder to replace the OPC. The current limitation of geopolymer concrete, it only can be produce in precast concrete industries. This case study is conducted to find a retarder that can slow the reaction of geopolymer so it can be transferred from mixture plant and can be cast in situ at site. Natural based retarders that proposed to use in this case study are sucrose and citric acid. The percentage of retarder were used are 0%, 1.5% and 2.5%. Not only focusing on that matter, this case study also investigating about the strength of 50mm x 50mm x 50mm cube that has been exposed to different type curing condition, ambient and oven (60^{o}). Compressive tests (ASTM C109M) were conducted after 1 day, 7 day, 28 day and 56 day. Furthermore, flow table test (ASTM C1437) also were conducted to measure the flow ability of fresh geopolymer mortar. After that, porosity test (ASTM C642) also were conducted to hardened geopolymer mortar to find out the percentage of porosity of the cube. Lastly, fresh geopolymer paste will undergo vicat test (ASTM C191) to measure the setting time of the paste. Total sample consist 140 hardened mortar and 5 fresh geopolymer paste sample for vicat test. The result of compressive strength between 1.5% sucrose and control sample has shown no significant different, so the strength is as good as control sample.More retarder added to the geopolymer mortar, more it will affected the compressive strength. Increasing citric acid will only accelerate the reaction of geopolymer paste. On the other hand, increasing of sucrose will retarded and slow the reaction of geopolymer paste.

ABSTRAK

Geopolimer itu telah diperkenalkan oleh Joseph Davidovits sebagai pengikat baru untuk menggantikan OPC. Batasan geopolimer ialah hanya boleh menghasilkan dalam industri konkrit pratuang. Kajian kes ini dijalankan untuk menguji pelambat yang di cadangkan dan menetukan yang boleh memperlahankan tindak balas geopolimer supaya ia boleh dipindahkan dari kilang campuran dan boleh dibawa ke tapak pembinaan. Pelambat semulajadi yang dicadangkan untuk digunakan dalam kajian kes ini adalah sukrosa dan asid sitrik. Peratusan pelambat yang digunakan adalah 0%, 1.5% dan 2.5%. Data kajian ini juga merangkumi tentang kekuatan 50mm x 50mm x 50mm kiub yang telah terdedah kepada suhu yang berlainan jenis, iaitu suhu bilik dan ketuhar (60^o). Ujian mampatan (ASTM C109M) yang telah dijalankan selepas 1 hari, 7 hari, 28 hari dan 56 hari. Tambahan pula, kebolehkerjaan mortar geopolimer di uji menggunakan ASTM C1437 . Selepas itu, keliangan ujian juga telah dijalankan untuk mortar geopolymer keras untuk mendapatkan nilai peratus keliangan kiub menggunakan ASTM C642. Akhir sekali, pes geopolymer segar akan menjalani ujian vicat (ASTM C191) untuk menyukat masa untuk pes geopolimer mengeras. Jumlah sampel terdiri 140 mortar kiub dan 5 geopolimer pes segar sampel untuk ujian vicat. Hasil daripada kekuatan mampatan antara sukrosa 1.5% dan sampel kawalan telah menunjukkan tiada perbezaan yang signifikan, maka kekuatannya adalah sama baik seperti sampel kawalan. Semakin banyak pelambat ditambah kepada mortar geopolimer, ia akan memberi kesan kepada kekuatan mampatan. Pertambahan asid sitrik hanya akan mempercepatkan tindak balas pes geopolymer. Sebaliknya, meningkatkan sukrosa akan melambatkan tindak balas pes geopolymer.

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LIST OF ABBREVIATION

OPC	=	Ordinary Portland cement
CO_2	=	Carbon Dioxide
TNB	=	Tenaga Nasional Berhad
ASTM	=	American Society for Testing and Materials
MPa	=	Mega Pascal
Na_2SO_3	=	Sodium silicate
NaOH	=	Sodium hydroxide
Al	=	Aluminium
kg/m^3	=	Kilogram per meter cube
g/m^3	=	Gram per meter cube
^oC	=	Celsius
s	=	Seconds
h	=	Hour
g	=	Gram
Kg/m^3	=	Kilogram per meter
N	=	Newton
N/mm^2	=	Newton per millimeter square
mm	=	Millimeter
kN	=	Kilo newton
Al_2O_3	=	Aluminium Trioxide
SiO_2	=	Silica dioxide
P_2O_5	=	Phosphorus Oxide
K_2O	=	Potassium Oxide
CaO	=	Calcium Oxide
TiO_2	=	Titanium Dioxide
Fe_2O_3	=	Iron Trioxide

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CHAPTER 1

INTRODUCTION

1.1 Background

The Important ingredient in a mixture to produce concrete or mortar is a well-known Portland cement. All places around the world have used this material in every construction building, bridge and many other concrete structures. It will grow and will be used alongside the urbanization. However, several problems about Portland cement concrete are related to its durability and carbon dioxide emission. Production of Portland cement, it will contribute to the increasing percentage of greenhouse emissions many concrete structures have shown serious deterioration, way before their intended service life, especially those constructed in a corrosive environment (Mehta,1997).

The production of ordinary Portland cement (OPC) also can harm the environment because from the production of the OPC releases large amount of carbon dioxide (CO_2) to the atmosphere that significantly contributes to greenhouse gas emissions. This is because one ton of carbon dioxide gas is released into the atmosphere for every ton of OPC produced. In the year 1995, the global production of ordinary Portland cement was about 1.4 billion tonne, thus emitting about 1.4 billion tonne of carbon dioxide to the atmosphere (Malhotra, 2004).

In order to reduce these issues from getting more serious, Joseph Devidovits developed inorganic polymeric material in year 1978 and use the term "Geopolymer" at 1990 to become the identity of this material. He introduced a new material that can be used as alternative binder to cement. The term "Geoploymer" is used because of its reaction between alkaline liquid and geological based source material (fly ash). The reaction product from this material can be used to bind fine aggregate, to formed mortar and also to bind coarse aggregate and fine aggregate to form concrete. (Davidovits, 1987,1990). From the test that has been conducted by Joseph Davidovits, geopolymer has the potential to replace Ordinary Portland Cement concrete and produce fly ash-based Geopolymer concrete with excellent physical and mechanical properties.

When it comes to comparison between Ordinary Portland Cement (OPC) and inorganic polymeric material as known as Geopolymer, it has many differences. From the test that has been carried out by Wallah and Rangan, geopolymer has an excellent durability properties in a study conducted to evaluate the long term properties of fly ash Geopolymer. Then, geopolymer has shown other excellent properties such as a high early strength, low shrinkage, high resistance to freezing and thawing, sulphate attack and corrosion (Davidovits, 1987, 1990).

Organic admixture are the great interest in concrete technology because it can longer the setting time and increase the workability without sufficiently affecting the long term mechanical properties of the concrete. (M.R Rixom, 1978). The reason of admixtures is added to geopolymer concrete at the mixing stage to improve its properties, such as flowability and/or setting time behavior. Fly ash based geopolymer concrete has the problems of low workability and rapid setting time. Proposed retarders of this case study are acid citric and sucrose. Acid citric is a well-known retarder for concrete. Among the carboxylic acids, citric acid has been found to be one of the most effective's retarder for (OPC) concrete (N.B. Singh et al, 1986). For sucrose it has been used in geopolymer concrete. It shows the positive impact to the geopolymer concrete by retarding it and prolongs the setting time also increase the flow ability.

1.2 Problem statement

Construction developments are increasing around the world every year. It will contribute to the increasing the usage of concrete and from that reason, the production of Portland cement will also increase. Therefore, the need of environmental friendly construction material is essential to produce a more sustainable structure that will not causing the environmental problem.

The other problem that leads to this study is the hardening process of geopolymer setting time is too fast, and cannot be transported to construction site. So, the limitation of geopolymer concrete is it only can be made in precast concrete industry. The solution to this problem is by using retarder that will be added to geopolymer mixture. But, the available commercial retarders that have been used by researchers in geopolymer area are not compatible with fly ash based geopolymer concrete, even though these retarders have performed perfectly in OPC based concrete. Suitable retarder is needed to support the reaction of fly ash based geopolymer concrete, while enhancing the workability of fresh geopolymer concrete. Therefore, citric acid and sucrose are proposed as the natural based retarders for this study.

1.3 Aim of study

This study is carry out to examine and observe the effect of non-commercial retarder such as citric acid and sucrose to the compressive strength on 1^{st} day, 7^{th} day, 28^{th} day, and 56^{th} day, the setting time for the geopolymer paste, and the total porosity of hardened geopolymer mortar. The retarders that are added into the mixture are 1.5% and 2.5% based on fly ash. On the other hand, 0% of retarder will be used as the control sample for the comparison.

1.4 Objectives of study

There are a few objectives that need to be achieved in this case study:

a. To determine the effect of citric acid and sucrose in the setting time of fresh fly ash based geopolymer paste.

b. To determine the flowability of geopolymer mortar with the inclusion of citric acid and sucrose.

c. To obtain the compressive strength of hardened fly ash based geopolymer mortar with the inclusion of citric acid and sucrose

d. To attain the total porosity of fly ash based geopolymer mortar with the inclusion of citric acid and sucrose.

1.5 Scope of study

The scope of study for this research is basically to study about the engineering properties of geopolymer paste and geopolymer mortar based on fly ash with the inclusion with non-commercial retarder such as sucrose and citric acid. The percentage of proposed retarder that used in this case study is 1.5% and 2.5% each retarder.

The setting time of vicat test is measured on geopolymer paste and flowability of geopolymer mortar was tested by using flow table test. This research also done to investigate the strength of geopolymer mortar also testing of compressive test will be carry out on day 1, day 7, day 28 and day 56. Sample of 0% retarder also will be produce to be compare with the sample that been added with retarder. The hardened mortar will be carrying out porosity test to find out the total porosity of the paste and the mortar. After that, two different curing conditions will be used in this case study, ambient and oven environment to be specific at 60^{o} c temperature.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In peninsular Malaysia, there are 4 famous electric power plants that use a coal (coal fired) as a power material for generate electricity to the state. There are at Perak, Johor, Selangor and Negeri Sembilan. The private sector is building a coal-fired power plant at Johor and another private sector group is building another plant at Negeri Sembilan. TNB's electric power plant in Perak by using coal fired to produce electricity. The result from burning coal, it will produce by product as known as waste material, 80% of product will become fly ash and remain 20% of product is bottom ash. To control fly ash and dust hovering in the atmosphere, recipient's electrostatics was built and used for trapping 99% of ash and dust.

This waste material will increase in the future because of the increasing population in Malaysia. Might be, in the future there will no place to dump this waste material. In order to make sure that this waste material not becoming one of big problem to our country, the waste material must be recycle, by reusing the waste material in construction, and after a lot of research, this waste material has potential to replacing Portland cement, and has a lot of advantage to human and environment better than Portland cement.

Other than that, Cement is one of major construction materials used in modern building and infrastructure around the world. According to a research conducted by Sutiyono, Indonesia, as a developing country, consumed cement at about 41 million tonne in 2009 and this number represents an increase of around1.5% in comparison to that of 2008. It is projected that the consumption of cement will be 46.5 million tonne in 2011 (Sutiyono, 2009). The increase in cement consumption will raise environmental concern.

Manufacturing of cement can impact on environment and will caused two environmental parameters for example climate change and fossil fuel depletion for the following reasons: in the first, the production of 1 tonne of cement directly generates 0.55 tonne of chemical CO_2 and requires the combustion of carbon-fuel to yield another 0.45 tonne of CO_2.

As the need of cement is increased, so the contribution of CO_2 emission from cement manufactures is also increased. In the 1980, the rate of the world-cement production already exceeded the rate of atmospheric CO_2 concentration. This could be interpreted as the rate of CO_2 emission produced from cement industries surpassed that from other human activities that produce major CO_2 emission i.e. energy consumption and transportation (Davidovits,1994). The manufacturing of OPC requires the burning of large quantities of fuel and decomposition of limestone, resulting in significant emissions of carbon dioxide (Kong and Sanjayan, 2008).

In the second, the production of cement requires a lot of energy to heat the clinker up to 1500°C. The amount of coal required to manufacture one tonne of cements between 100 kg and about 350 kg depending on the process used (Neville and Brooks, 1987). With projected cement consumption in Indonesia for 2011 is about 46.5 million tonne; it means it requires at least 4.65 million tonne of coal for cement manufacturing process. Clearly, this number of coal consumption will directly be a factor in fossil fuel depletion.

Being concern with those environmental impacts, attempt had been done to reduce the use of cement by replacing part of the cement with other cementitious materials to form blended cement. As such, geopolymer concrete had been introduced to reduce the above problem. Geopolymer concrete also showed good properties such as high compressive strength, low creep, good acid resistance and low shrinkage (Lodeiro et al., 2007).

2.2 History of Geopolymer

The historical development of alkali activated cement started at 1930, when Kuhl investigating about the setting behavior of mixture of ground slag powder and caustic potash solution. After that, another experiment of reactivity measured of slag using caustic potash solution. At 1940, Purdon do another experiment on clinkerless cements that include slag and caustic soda produces by base and and alkaline salt. (Caijun Shi et Al, 2006)

In 1957, producing of binders using low basic calcium or calcium-free aluminosilicate (clays) and solution of alkali metal had first discovered by Glukhovsky. The binder is known as 'soil cements' and the 'soil silicates' as the corresponding concrete. (Glukhovsky, 1959).

In 1981, France citizen known as Davidovits produce a binder by mixing alkali with burnt mixture of kaolinite, limestone and dolomite (Davidovites 1981). The binders have been called 'Geopolymer' by Davidovits because of the polymeric structure inside the binders. Davidovits also used trademark such as Pyrament, Geopolycem and Geopolymite for the binders. This type of material that had been found by Davidovits is same as alkaline binding system that has been discovered by Glukhovsky.

2.3 The Geopolymer Terminology/ Geopolymer Reaction

In geopolymer reaction, alumina-silicate binders are called inorganic geopolymeric compounds, since the geopolymeric cement obtained is the result of an inorganic polycendensation reaction. That process is called geopolymerization. The reaction of geopolymerization works according to this empirical formula:

$$M_n[-(SiO_2)_z - AlO_2]_n wH_2O$$

M = cation (Na, Ca)

n = the degree of polycondensation

z = 1,2,3 or >>3

Where: M = the alkaline element or cation such as potassium, sodium or calcium, the symbol – indicates the presence of a bond, n is the degree of or polymerization; z is1,2,3, or higher, up to 32. The framework $[-(SiO_2)_z - AlO_2]_n$ is called sialate stands for silicon-oxo-aluminate building unit. The sialate network consists of SiO4 and AlO4 tetrahedras linked by sharing all oxygen atoms. Positive ions (Na^+, Ca^{2+}, etc) will balance the negative charge of Al in 4-fold coordination (Davidovits, 2005). This happens to complete the electron valence of Al.

For the chemical designation of geopolymers based on silico-aluminates, poly(sialate) was suggested. The amorphous semi-crystalline of three dimensional silico-aluminate were illustrated as in figure 1.

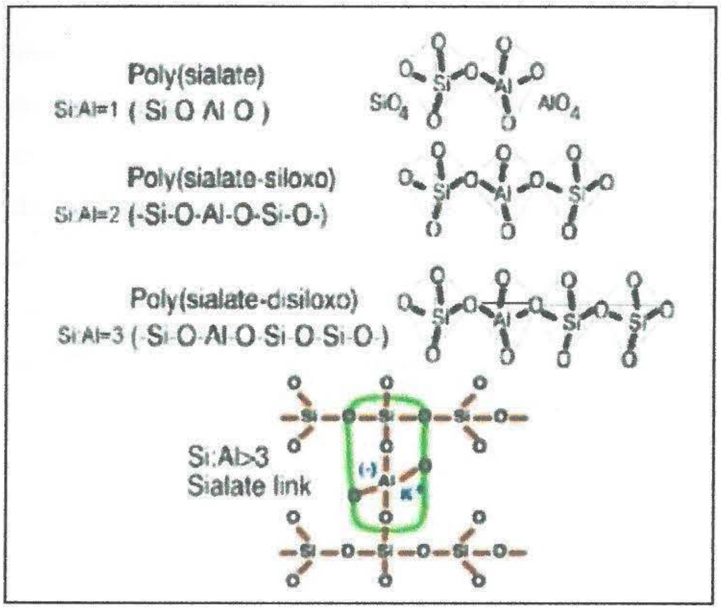

Figure 2.1 : The geopolymer terminology (Davidovits, 2005)

There are three types of geopolymer structures, for example, poly(sialate) (-Si-O-Al-O-), poly(sialate-siloxo) (Si-OAl-O-Si-O-) and poly(sialate-disiloxo) (-Si-O-Al-O-Si-O-Si-O-). Geopolymers that have poly(sialate-siloxo) and poly(sialate-disiloxo) structures are more rigid, more stable, and stronger than poly(sialate) structures .

Researchers also stated that increasing the crystallinity of the geopolymer products increased their compressive strength.

2.4 Geopolymer

Geopolymer materials represent an innovative technology that is generating considerable interest in the construction industry, particularly in light of the ongoing emphasis on sustainability. From the first industrial research efforts in 1972 at the Cordi-Gĕopolymĕre private research laboratory, Saint-Quentin, France, until the end of 2006, hundreds of papers and patents were published dealing with geopolymer science and technology (Davidovits, 2008). There are nine different classes of geopolymers, but the classes of greatest potential application for transportation infrastructure are comprised of aluminosilicate materials that may be used to completely replace portland cement in concrete construction (Davidovits, 2008).

Organic polymer has a major element consisting of carbon atoms. Substances with giant molecules composed of atoms other than carbon and linked together mainly by covalent bonds is called inorganic polymer. For example, when Si, Al, and O are linked to make up the repeating units such as (-Si-O-Al-O-), these amorphous-semicrystalline inorganic polymers are called geopolymers. Geopolymer are amorphous to semi-crystalline three dimensional alumina silicate polymers similar to zeolites (Davidovits, 1999). Geopolymer consist of polymeric silicon-oxygen-silicon framework with silicon and aluminium tetrahedral alternately linked together in three direction by sharing all oxygen atoms. Many studies have shown that geopolymer possess and outstanding mechanical properties.

Geopolymers are made from source material with silicon (Si) and Aluminium (Al) as a major compound in the contents. So in that case, it can be made from fly ash, waste product of coal-fired power station, as the source materials (Hardjito, Wallah, & Sumajouw, & Rangan, 2004a). Furthermore, geopolymers possesses excellent mechanical properties which does not dissolve in acidic solution and does not generate any hazardous alkali-aggregate reaction even with alkali content as high as 9.2 % (Davidovits, 1999).

Although the mechanism of polymerization is yet to be fully understood, a critical feature is that water is present only to facilitate workability and does not become a part of the resulting geopolymer structure. In other words, water is not involved in the chemical reaction and instead is expelled during curing and subsequent drying. This is in contrast to the hydration reactions that occur when Portland cement is mixed with water, which produce the primary hydration products calcium silicate hydrate and calcium hydroxide. This difference has a significant impact on the mechanical and chemical properties of the resulting geopolymer concrete, and also renders it more resistant to heat, water ingress, alkali–aggregate reactivity, and other types of chemical attack (Davidovits 2008; Lloyd and Rangan 2009).

In the case of geopolymers made from fly ash, the role of calcium in these systems is very important, because its presence can result in flash setting and therefore must be carefully controlled (Lloyd and Rangan 2009). Moreover, the temperature during curing is very important, and depending upon the source materials and activating solution, heat often must be applied to facilitate polymerization, although some systems have been developed that are designed to be cured at room temperature (Hardjito et al. 2004; Davidovits 2008; Rangan 2008; Tempest et al. 2009).

Geopolymer use as a binder same as cement paste, to produce mortar or concrete. The geopolymer paste binds the loose fine aggregates and other unreacted materials together to form the geopolymer mortar. The manufacture of geopolymer concrete is carried out using the usual concept of concrete technology method. In geopolymer mortar, fine aggregates occupy the largest volume same as when mix it with Portland cement. The silicon and the aluminium in the fly ash are activated by a combination of sodium hydroxide and sodium silicate solutions to form the geopolymer paste that binds the aggregate and others unreacted materials.

Geopolymers are environmental friendly materials which do not emit greenhouse gases during polymerization process. Besides that, to produce geopolymers it only need moderate energy compare to Portland cement. In this case, it can reduce the effect of global warming and energy saving. It is well known the production of Portland cement will be emitted a great amount of carbon dioxide, which is one reason of the global warming. Studies has shown that one ton of carbon dioxide gas is releases into the atmosphere for every ton of Portland cement which is made anywhere in the world.

To be compared, geopolymer cement is produced very different way than Portland cement. About less 3/5 energy was required and 80% - 90% less CO_2 is generated for the production of geopolymer than that of Portland cement. Thus it is a great significance in environmental protection for the development and application of geopolymer cement (Zongjin Li, 2002).

2.4.1 Alkaline activator

The common materials used as alkaline solution in producing fly ash based geopolymer are sodium silicate (Na_2SO_3) and sodium hydroxide (NaOH). Usually either of this material was mixed with sodium hydroxide to produce the alkaline solution and the molarity (M) of alkaline solution is 7 to 10 M (M.Mustafa Al Bakri, 2010). But for this study 8M of solution will be used. The alkaline solution was prepared a day before it is mix with fly ash. Then, the materials are mixed together with fly ash and fine aggregates to form mortar. Sodium is widely use compare to the potassium that have limited due to the availability and cost.

Figure 1 below shows the dissolution process of the Si and Al occurs when the fly ashes are mix with the alkaline solution. Then the higher molecules condense in a gel form and the alkali attack on the surface of particle, and then expand to larger hole, exposing smaller particles whether hollow or partially filled with other yet smaller ashes to bidirectional alkaline attack from the outside in and from the inside out. Consequently, reaction product is generated both inside and outside the shell of the sphere, until the ash particle is completely or almost completely consumed (Pacheco-Torgal *et al.*, 2008).

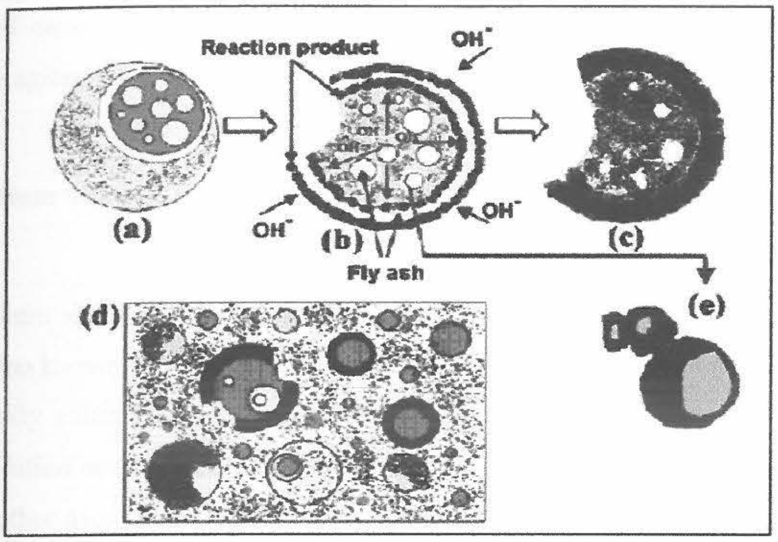

Figure 2.2 : Descriptive model of the alkali activation of fly ash (Pacheco-Torgal *et al.*, 2008).

2.4.1.1 Sodium Hydroxide/ Caustic Soda (NaOH)

Sodium hydroxide (NaOH) also known as a caustic soda. Pure sodium hydroxide is a white solid available in flakes, pellets, granules, and as a 50% saturated solution. It is hygroscopic and readily absorbs carbon dioxide from the air, so it should be stored in an airtight container. It is very soluble in water with liberation of heat. Molten sodium hydroxide is also a strong base, but the high temperature required limits applications. For this experiment, solid caustic soda is required to have better result.

In factory, solid caustic soda is obtained by cooling molten caustic soda, from which all the water has been evaporated. After that, flake caustic soda is made by passing molten caustic soda over cooled flaking rolls to form of controlled particle size (Caijun Shi, 2006). In cement and concrete production Caustic soda can be used as an accelerator of cement hydration. However, it results in a decrease of strength after 7 to 14 days of hydration. For most ultimate uses, caustic soda is used in solution form and the anhydrous solid caustic soda must be dissolved. Because of very high heat of solution, a rapid temperature increase can result in dangerous boiling and/or spattering if caustic soda is added to a solution too fast, or if the solution is not sufficiently agitated or if added to a hot or cold liquid.

2.4.1.2 Sodium Silicate (Na_2SO_3)

Sodium silicate is the common name for a compound sodium metasilicate, Na_2SiO_3, also known as water glass or liquid glass. Sodium silicate is a white powder that is readily soluble in water, producing an alkaline solution. It is available in aqueous solution and in solid form and is used in cements, passive fire protection, and many other uses. From research that has been conducted, soluble alkali silicates are the most effective activators for most alkali-activated cementing materials.

The sodium silicate glass is obtained by melting primary sand and sodium carbonate. Then the glass is dissolved in an autoclave at under suitable steam pressure. Sodium silicate glass components can be designated as Na2O· nSiO2 – where *n* is the ratio of the components and fall in the practical range from 0.4 to 4.0 (Caijun Shi, 2006).

Sodium silicate was widely used as an accelerator for concrete. Sodium silicate is the most effective alkaline activator for many cementing systems same as caustic soda (NaOH). With the development of a new technology for producing hydrated silicate powders, the applications of soluble glass in construction have greatly expanded, such as dry glue mixtures, adhesives, oil well cements, and special cements for immobilization by cementation of different hazardous, toxic and radioactive wastes, acid resistant concrete, etc. (Korneev and Brykov 2000, Aborin *et al.* 2001).

2.4.2 Source of Material

Geopolymers generally are produced by activation of a source material. The strength of the geopolymer depends on the nature of source of material. The source material used for geopolymerisation can be a single material or a combination of several types of materials. (Davidovits J, 2005) .