STUDY OF SILICA GEL AS SELF-HEALING AGENT IN GEOPOLYMER MORTAR EXPOSED TO EXTREMELY HIGH TEMPERATURE

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ABSTRACT

Geopolymer can be used to produce structural concrete without the consideration on the emission of carbon dioxide as what Portland cement did. Geopolymer are produced when alumino-silicate, like fly ash mixed with a strong alkaline solution. The production of geopolymer is more economical and sustainable than normal cement. Durability of a structure is one of the concern for the engineers. In order to maintain the strength characteristic of the geopolymer, way to prolong the lifespan and cater the durability problems caused by cracks after high temperature exposure. Presence of self-healing agent contributes to the enhancement on the strength characteristic of the geopolymer concrete after high temperature exposure. There are several type of self-healing agent which can be used in geopolymer, such as: Poly Methyl Acrylate, silica gel, tung oil,silicone and bacterial solution. Silica gel will be used for this research as a self-healing agent. The main objective of this research is to determine the strength performance of self-healing geopolymer mortar after high temperature exposure. This research is conducted along with the following sub-objectives which is to identify the suitability of silica gel as self-healing agent in geopolymer mortar after exposed to extremely high temperature and the effectiveness of silica gel as self-healing agent in geopolymer mortar. Samples were subjected to elevated temperature of 500, 600 and 700 ℃. The highest compressive strength achieved with the inclusion of silica gel in the specimen was 63.579 MPa which is higher than normal concrete. The compressive strength of the geopolymer mortar is also preserved after high temperature exposure. The performance of the geopolymer concrete is enhanced with the presence of the self-healing agent as the micro cracks are filled. The compressive strength of geopolymer was preserved even after exposure to 500 ℃ in the furnace for 30 minutes. Samples showed that the compressive strength decreased exponentially from 600 ℃ onwards which indicated geopolymer started to fail structurally. At 500 ℃, the compressive strength did not have significant difference where there are only slight reduction in the specimens. As a conclusion, the objectives of this research have been fulfilled. Silica gel is suitable for the self-healing mechanism to take place. However, the silica gel should be replaced with non-commercial silica gel to ensure that the effect of self-healing mechanism take place with better framework produced through the reaction of the silica gel with the geopolymer.

ABSTRAK

Geopolimer boleh digunakan untuk menghasilkan konkrit tanpa pertimbangan atas pelepasan karbon dioksida seperti apa simen Portland lakukan. Geopolimer dihasilkan apabila alumino-silika, seperti fly ash dicampur dengan larutan alkali yang kuat. Pengeluaran Geopolimer lebih menjimatkan dan tahan lasak berbanding dengan simen biasa. Ketahanan struktur merupakan salah satu factor kebimbangan bagi jurutera. Dalam usaha untuk mengekalkan ciri-ciri kekuatan daripada Geopolimer, cara untuk memanjangkan jangka hayat dan memenuhi masalah ketahanan yang disebabkan oleh retak-retak yang terjadi akibat pendedahan kepada suhu tinggi. Kehadiran ejen pemulihan diri menyumbang kepada peningkatan pada ciri kekuatan konkrit Geopolimer selepas pendedahan suhu tinggi. Terdapat beberapa jenis penyembuhan diri ejen yang boleh digunakan dalam Geopolimer, seperti: Poli Methyl Akrilat, gel silika, minyak tung, silikon dan pendekatan bakteria. Silika gel akan digunakan untuk kajian ini sebagai agen penyembuhan diri. Objektif utama kajian ini adalah untuk menentukan prestasi kekuatan penyembuhan mortar Geopolimer selepas pendedahan kepada suhu tinggi. Kajian ini dijalankan bersama-sama sub-objektif dengan yang berikut iaitu untuk mengenal pasti kesesuaian gel silika sebagai agen penyembuhan diri dalam Geopolimer mortar selepas terdedah kepada suhu yang sangat tinggi dan keberkesanan gel silika sebagai penyembuhan diri ejen di Geopolimer mortar. Sampel tertakluk kepada suhu tinggi daripada 500, 600 dan 700 ° C. Kekuatan mampatan yang paling tinggi dicapai dengan kemasukan gel silika di dalam spesimen itu adalah 63,579 MPa yang lebih tinggi daripada konkrit biasa. Kekuatan mampatan mortar Geopolimer juga dipelihara selepas pendedahan suhu tinggi. Prestasi konkrit Geopolimer yang dipertingkatkan dengan kehadiran agen penyembuhan diri sebagai retak mikro dipenuhi. Kekuatan mampatan Geopolimer dipelihara walaupun selepas terdedah kepada 500 °C dalam dapur selama 30 minit. Sampel menunjukkan bahawa kekuatan mampatan menurun dengan pesat dari 600 ° C dan seterusnya yang menunjukkan Geopolimer mula gagal struktur. Pada 500 °C, kekuatan mampatan tidak mempunyai perbezaan yang ketara di mana terdapat hanya sedikit penurunan dalam spesimen. Kesimpulannya, objektif kajian ini telah dipenuhi iaitu gel silika sesuai untuk mekanisme pemulihan diri untuk mengambil tempat. Walau bagaimanapun, gel silika yang perlu diganti dengan gel silika bukan komersial untuk memastikan bahawa kesan mekanisma pemulihan diri berlaku dengan rangka kerja yang lebih baik dihasilkan melalui tindak balas gel silika dengan Geopolimer itu.

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LIST OF SYMBOLS

℃	Degree Celcius
%	Percent
Cm	Centimeter
kg/m^3	Kilogram per cubic meter
kg	Kilogram
mm	Millimeter
N/mm^2	Newton per square millimeter
kN	Kilo Newton

LIST OF ABBREVIATIONS

ASTM	America Society for Testing and Materials
BS	British Standard
MIX	Mixture
OPC	Ordinary Portland Cement
SHA	Self-Healing Agent
Na_2SiO_3	Sodium Silicate Solution
SiO2	Silicon Oxide

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Concrete is one of the most commonly used materials in constructions. Concrete is a type of composite material for construction which generally composed of cement, course aggregates fine aggregates and water. Ordinary Portland Cement (OPC) is widely used as a binder for concrete mixing (Sarker et al., 2014).The emission of greenhouse gases such as carbon dioxide, CO_2 into atmosphere from the manufacturing of cement is contributed to the greenhouse effect issues (Ganesan et al., 2014).

Therefore, an alternative binder is emerged in order to take care on the greenhouse gases emissions' issues. (Sarker et al., 2014). Research on geopolymer was initiated by Glukhovsky back in 1957. The development of a new binder material using inorganic materials is introduced by Joseph Davidovits in 1972 (Andri Kusbiantoro, 2012). There are several type of inorganic materials that can be used, for instance fly ash and steel fibre.

Although geopolymer concrete can be produced from a side variety of inorganic waste material, fly ash is considered one of the most effective geopolymer binders for concrete manufacturing. Fly ash based geopolymer concrete is a newly developed construction material which is more environmental friendly.

Fly ash is a coal combustion product which is the most prominent source material in geopolymer. The uses of fly ash are increasing throughout the years due to its amorphous alumina silica content and its availability is abundant around the world

(Andri Kusbiantoro, 2012). The study shown that the total amount of fly ash produced in the world is relatively distinct from the OPC production. The production amount for fly ash is 480 million tons and for OPC is 3.3 billion tons respectively (Oss HGV. Cement United States Geological Survey: Mineral Commodity Summaries 2011). Fly ash based geopolymer utilizes the alkaline solution to activate alumina and silica precursors from the source material and form the binding material which is aluminousilicate-based.

Presence of self-healing agent contributes to the enhancement on the strength characteristic of the geopolymer concrete after high temperature exposure. There are several type of self-healing agent which can be used in geopolymer, such as: Poly Methyl Acrylate, silica gel, tung oil,silicone and bacterial solution (Tittelboom et al.,2013). Silica gel will be used for this research as a self-healing agent. It is a kind of combustion based self-healing agent.

1.2 PROBLEM STATEMENT

Research on fly ash based geopolymer is gradually increased throughout the years. There is a trend that geopolymer concrete will be replacing conventional concrete as it is more environmental friendly and more cost effective. The dependable characteristic of geopolymer shows that it has a relatively high strength compared to the ordinary concrete.

However, crack occurs most of the time in concrete after a certain period. It occurs more significantly especially after an exposure of high temperature (Kong et al., 2009). It occurs in geopolymer concrete as well. Strength characteristic of a geopolymer concrete is reduced after high temperature exposure because the propagation of cracks increased. The lifespan of a geopolymer structure is shortened and the weakened structure is not able to provide its designed service duration. At worst, it will lead to a structural failure with undesired casualties or deaths, Hence, in order to cater the problems, a proposal of combustion based self-healing agent, silica gel is used.

Structures like tunnel or concealed structures have the tendency that will expose to high temperature as the heat is trapped. It is not very convenient and the maintainer is exposed to high risks when maintenance is needed in such area with high temperature. Geopolymer structures with self-healing attribute will heal the cracks whenever exposed to high temperature for a certain period. It will be an alternative for the construction of concealed areas where the maintenance is not able to access at ease.

Geopolymer does not have autogenous healing. Hence, when it exposed to extremely high temperature, non-evaporable water will leave the geopolymer. It will trigger shrinkage where it leads to cracking. As the time goes on, it will lead to failure. If this problem occur in the structure, it will cause damages and become a disaster to the environment. This research proposed is to study the inclusion of silica gel as self-healing agent as it is expected to heal the cracks in geopolymer when exposed to extremely high temperature.

1.3 OBJECTIVE OF RESEARCH

The main objective of this research is to determine the suitability of silica gel as self-healing agent in geopolymer after exposed to extremely high temperature. This research is conducted along with the following sub-objectives:

- To obtain the compressive strength and porosity of geopolymer containing silica gel after extremely high temperature exposure.
- To identify the effective extremely high temperature for silica gel as self-healing agent in geopolymer.

1.4 SCOPE OF RESEARCH

In order to achieve all the research objectives, a series of scope of works are considered and taken into account. This research is limited to the following considerations.Fly ash used is originated from coal-fire power station, Manjung, Perak. The geopolymer mortar cubes are molded in 50 x 50 x 50 mm and tested for compressive strength and porosity at age of 1 day and 28 days respectively. The geopolymer concrete cubes are left for one and half hour for self-curing before oven curing at 70 ℃ for 24 hours. High temperature exposure on the geopolymer concrete cubes at age of 28 days is set at 500 ℃, 600 ℃, and 700 ℃. Self-healing specimens are using the same mixture proportion with controlled specimens, but with additional 1 % silica gel. Self-healing agent used is silica gel which is a heat-based agent. Fine aggregates are prepared by using 5mm sieve. Fly ash is prepared by using 150 micrometer sieve.

1.5 RESEARCH SIGNIFICANCE

The use of silica gel as self-healing agent optimizes the performance of geopolymer concrete especially when exposed to the high temperature. The self-healing characteristic in geopolymer will prolong the lifespan and the durability in order to provide longer services. Besides, the compressive strength of the geopolymer concrete is also preserved after high temperature exposure. The performance of the geopolymer concrete is enhanced with the presence of the self-healing agent as the micro cracks are filled. At the same time, the effective extremely higher activation temperature for silica gel is identified after the research. The strength characteristic after the extremely high temperature is preserved as silica gel which is the self-healing agent melted inside the geopolymer mixture and fills the cracks.

Samples were subjected to elevated temperature of 500, 600 and 700 ℃. With the presence of silica gel as the self-healing agent added into the mixture, the expected outcomes were outlined. Effective extremely high temperature for activation of self-healing agent was determined and the racks in geopolymer mortar cubes were filled with self-healing agent after high temperature exposure. Besides that, width and propagation of cracks were reduced. Compressive strength of geopolymer mortar specimen was not much varying from controlled specimen after high temperature exposure and the strength characteristics and porosity were identified at different high temperatures.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This Chapter will discuss the literature review on the geopolymer. This chapter consists of two main sub-sections which are the self-healing mechanism and high temperature effect on the geopolymer. Impact on the environment is now a main concern throughout the nation. Many researches have been done in order to tackle the problem. Geopolymer is a more environmental friendly material which can be used in conctruction. This Chapter will present the background to the developments of self-healing fly ash based geopolymer.

2.2 GEOPOLYMER CONCRETE

Polymer is a type of large molecules that are made up of a series of repeating units which are call monomers. The properties of the material are made up by the molecular structure. Along with the global awareness and concern on the climate change, geopolymer has a higher attention from the researchers and industries due to its ability as a binder in structural application. This term was coined by Davidovits because of his researches on inorganic-polymer technologies especially for the industrial applications.

Geopolymer is a member of inorganic polymers' family. Its structure consists of series of Al and Si ions. The chemical composition of geopolymer is quite similar to natural zeolitic materials, but the microstructure is different (Xu and Van, 2000) Instead of crystalline microstructure, they have an amorphous microstructure.

It is formed when alumino-silicates is dissolved in a strong alkaline solution and precipitated in a harden stage. Generally, the polymerization process involves a chemical reaction which is fast under a highly alkaline condition. It results in a three-dimentional polymeric chain and ring structure which consist of Si-O-Al-O bonds (Davidovits 1999). The bond is as follows:

$$Mn\ [-(SiO_2)\ z–AlO_2]n\ .\ wH_2\ O$$

However, there is no clear mechanism of geopolymer setting and hardening to the date (Davidovits, 1999). The proposed mechanism of a geop polymer by Xu and Van Deventer (2000) is as below:

- Action of hydroxide ions dissolute the Si and Al atom from the source material
- Precursor ions transport or orientate or condense into monomers
- Setting or polycondensation / polymerisation of monumbers into polymeric structures

Geopolymer cement concrete has a very similar properties to Portland cement when they are formed under certain condition. Geopolymer makes use of the industrial waste such as fly ash because of its abundance to the quality produced. In another word, geopolymer makes good use of the waste material at the same time reducing the greenhouse gases emissions because it reduce the usage of cement.

2.2.1. FLY ASH

ACI Committee 232 (2004) defines that fly ash is the residue that finely divided which results from coal and is transported by flue gases from combustion zone to the particle removal system. Fly ash is relatively small compared to Portland cement, which range between less than 1 μm and 150 μm.

Fly ash utilization has significant environmental benefits, especially in concrete production industry, viz, better durability, reduction on energy used; lessen the production of greenhouse gases, and reduction of fly ash disposal (Hardjito D. 2005; ACAA, 2003).

2.2.2. SODIUM SILICATE

Alkaline activator is needed to activate the fly ash. Sodium-based activator is chosen because it is relatively cheap compared to Potassium-based activators. Sodium silicate is used as a bonding agent for the fly ash and aggregates to produce a geopolymer concrete (R.Anuradha et al. 2011).

2.2.3 AGGREGATES

Aggregates are used in geopolymer concrete because they give strength and durability to a concrete (Jeenu G. et al., 2012). There are two types of aggregates which are course aggregates and fine aggregates. They are categorized according to the size of the aggregates. The aggregates are sieved using different sieve size.

2.3 SILICA GEL

Silica gel also known as the synthetic amorphous silica. It appears in blue color and turns into pink solid when undergoes oxidation when it reacts with water or vapours. The molecular formula for silica gel is:

$$SiO_2.xH_2O + CoCl_2$$

Silica gel are often used as adsorbent or desiccant. Cobalt Chloride is impregnated in silica gel which act as a moisture indicator by changing the color from deep blue to pink then to pale blue.

However, silica gel is harmful and will lead to certain hazards to our health for example irritation on skin contact due to abrasive actions.

Figure 2.1: Silica Gel

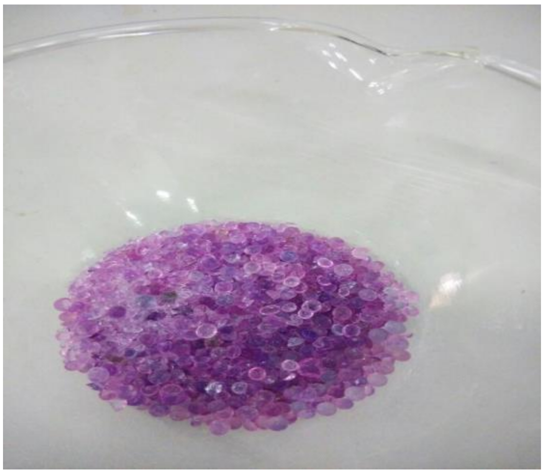

Figure 2.2: Silica Gel after oxidation

The self-healing mechanism occurs when this thermoplastic polymer is melted into crack areas and it will mechanically trigger the interlocking with the surrounding materials, whereas the cracks are filled and retain the strength characteristic of the geopolymer (Blaiszik et al., 2010).

2.6 COMPRESSIVE STRENGTH

Compressive strength is mandatory to be considered and ensured that it is up to standard. This is to make sure the application of the concrete in construction is able to meet the design requirement as well as to understand the strength development. Generally compressive strength of a geopolymer will be higher than conventional concrete. Hardjito & Rangan (2005) studied that compressive strength and workability of geopolymer concrete is closely influenced by the properties of material that make up the geopolymer.

Mix design and curing regimen of geopolymer can be optimized by relating the strength development of the geopolymer with the energy consumed for fly ash activation and concrete curing at elevated temperature (Tempest et al., 2009). According to Harjito and Rangan (2005), when superplasticizers are used, the concrete produced has the compressive strength between 44 to 90 MPa.

The curing process and hardening for geopolymer is different from the Portland cement. Geopolymers' strength tends to increase after curing and exposed to extremely high temperature. The temperature is vary from room temperature to 100 ℃ depending on the strength requirement. Temperature has an effect on the setting time, porosity and the strength development of a geopolymer (Tempest et al,.2009).

Selection of activating solution also will affect the strength development of the geopolymer. Sodium Hydroxide (NaOH) is more preferable than potassium hydroxide (KOH) because it has a greater efficiency to liberate the aluminate and silicate from the sources materials. It will have a better solubility as the alkali concentration is increased, yet excessive alkali hydroxide or silicate contain will retard the strength development. There is an unpublished research at UNCC shows that mixture which contains activating solution more than the NaOH/fly ash ratios greater than 0.16 are hard to work with. This is because the activator exhibit poor workability.

2.7 WATER POROSITY

Porosity can be referred to water absoption or in another word, the pore volume in a hardened concrete (Ferraro & Nanni, 2012). The performance of a geopolymer is closely related to the porosity. The more pores in the specimen will result in a lower compressive strength of the specimen.

2.8 SELF HEALING CONCRETE

Self-healing concrete is a concrete that will filled the cracks by its own. Cracks are commonly happened in concretes. Cracks play a role which is very important in serviceability limit of the concrete. Visible cracks can be repaired while non-visible cracks will be a problem for maintenance. Cracks endanger the strength and durability of concrete structures as it will lead to greater damage to the whole structure. Crack control methodology might overcome the concrete structures' serviceability limit which affected by the cracking (Ahn et al., 2009).

Self-healing is a well-known concrete phenomenon as it possesses natural autogenous healing properties (Kim Van et al., 2013). Self-healing capability is significantly affected by the materials especially aluminosilacate and different type of calcium composite materials.

2.6.1 AUTOGENEOUS HEALING BEHAVIOUR

The healing mechanism is attributed to the hydration of cement grains with carbonation that are not hydrated. The bonding materials formed include crystals made up of calcium carbonate and calcium hydroxide. Nevertheless, Ahn and Kishi (2009) also mentioned that it is generally recognized the unhydrated cement grains will affect the recrystallization of cracked concrete. The main self-healing phenomena for plain concrete is controlled by the amount of water presence in the mixture. Therefore, recrystallization of cracked concrete can be investigated when self-healing ability is given to a cementitious composite with normal or high water/cement ratio. Geo-materials are incorporated as partial cement replacement in order to investigate the self-healing properties.

According to Ahn and Kishi (2009), there are few researchers had observed the cementitious product formation like Aft, AFm and $CaCO_3$ in cracks and there are calcium hydroxide crystal found in the cracked concrete. From the research done, it was observed that the crack with 0.2 mm initial width was healed after 28 days. The rehydration products that were found in between the cracks were observed after 14 days. As of the result of 200 days healing period, the cracks were self-healed perfectly between the rehydration products.

The recovery in the structure which included the self-healing phenomena, for instance swelling and expansion effect, and re-crystallization. However, cracked aggregate is considered that they do not heal on their own.

2.6.2 CAPSULE BASED SELF-HEALING

Capsule based self-healing agent can be triggered by several ways which include damage, contact with moisture or air, or due to heating (Kim Van et al., 2013). Capsule based agent may be in spherical shape or cylindrical shape (Figure 2.1A & 2.1B)

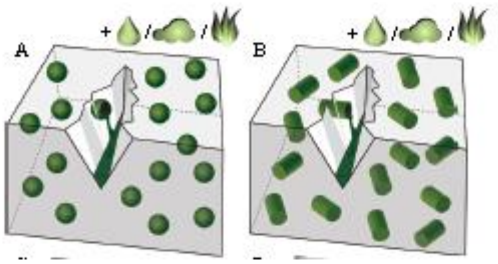

Figure 2.3 Shape of self-healing capsule

Source: Kim Van et al. 2013

Cailleux and Pollet (2009) explored that capsule based healing agent was destroyed during the mixing of concrete repair mortar which result in releasing the encapsulated agent. Upon crack, the specimen needs to be heated up so that the self-healing agent would start filling inside the cracks.

Healing agent's viscosity is an important parameter that will affect the healing effect of the agent. The viscosity shall not be too high so that it is able to fill the crack when needed, yet low viscosity will make the agent to leak out and become useless due to surrounding matrix's absorption (Cailleux and Pollet, 2009).

The agent should not cure rapidly but at a pace where it can heal the cracks completely.

2.7 POLYMERIZATION

Geopolymers are the product of polymerization of aluminate and silicate species that are dissolved from their original sources at high pH with the presence of alkali metals. There are 3 types of structure that a geopolymer can be expressed, which are poly(sialate) (-Si-O-Al-O-), poly(sialate-silixo) (Si-O-Al-Si-O) and poly(sialate-disiloxo) (Si-O-Al-Si-O-Si-O). The major difference between geopolymers and Portland cement is calcium in terms of chemical composition.

Geopolymerization was the reaction undergone by aluminosilicates in a highly concentrated alkali hydroxide or silicate solution, forming a very stable material called geopolymer having amorphous polymeric structures with interconnected Si–O–Al–O–Si bonds. According to (Duxson et al.2007) and (Dimas et al.2009), when there was dissolution of aluminosilicate materials with a strong alkaline solution, geopolymerization process was occurred together with the formation of silica–alumina oligomers in which the polycondensation of the oligomeric species to form inorganic polymeric material, and bonding of un-dissolved solid particles in the final geopolymeric structure. Sodium silicate (Na_2SiO_3) is an activating solution that is more preferable because of its soluble silicate content. It tends to increase the polymerization reaction rate.

2.8 ELAVATED TEMPERATURE

According to Kong et al. (2009) geopolymer undergoes high early strength development. However, strength reduction occurs when the specimen is exposed to 600 ℃. In comparison, elevated heat affects more on larger specimens than the specimens that are smaller in size.

Fly ash based geopolymer shows a good retention of strength after high temperature exposure. The residual fly ash particles can remain stable although exposed to extremely high temperature (Zhang et al., 2014). In order to induce significant changes to the silica gel, elevated temperature that is more than 300 ℃ is necessary (Patel et al., 2013). The minimum temperature is closely related to the thermal stability of the silica gel.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 INTRODUCTION

Research methodology is a systematic way that allows us to collect relevant data and information needed for the research project. It also can be defined as the process flow for a researcher to tackle and solve the problems he might encounter in a research. Hence, the research can be carried out in theoretical and systematic procedures.

This research was conducted in laboratory. The testing included compressive strength test and also the porosity test on the geopolymer mortar. Experimental investigation of the mix proportions were conducted according to the presence of silica gel as self-healing agent in the specimen. Presence of silica gel in the specimen indicated the healing mechanism in the specimen. Compressive strength and porosity of the geopolymer were measured at 1 and 28 days. Specimens of mortar cubes were 50mm x 50mm x 50mm in size. Different sets of specimen were heated at 500, 600 and 700 ℃ before tested for compression and porosity. Controlled specimens with and without inclusion of silica gel were tested without exposed to elevated temperature.

3.2 FLOW CHART

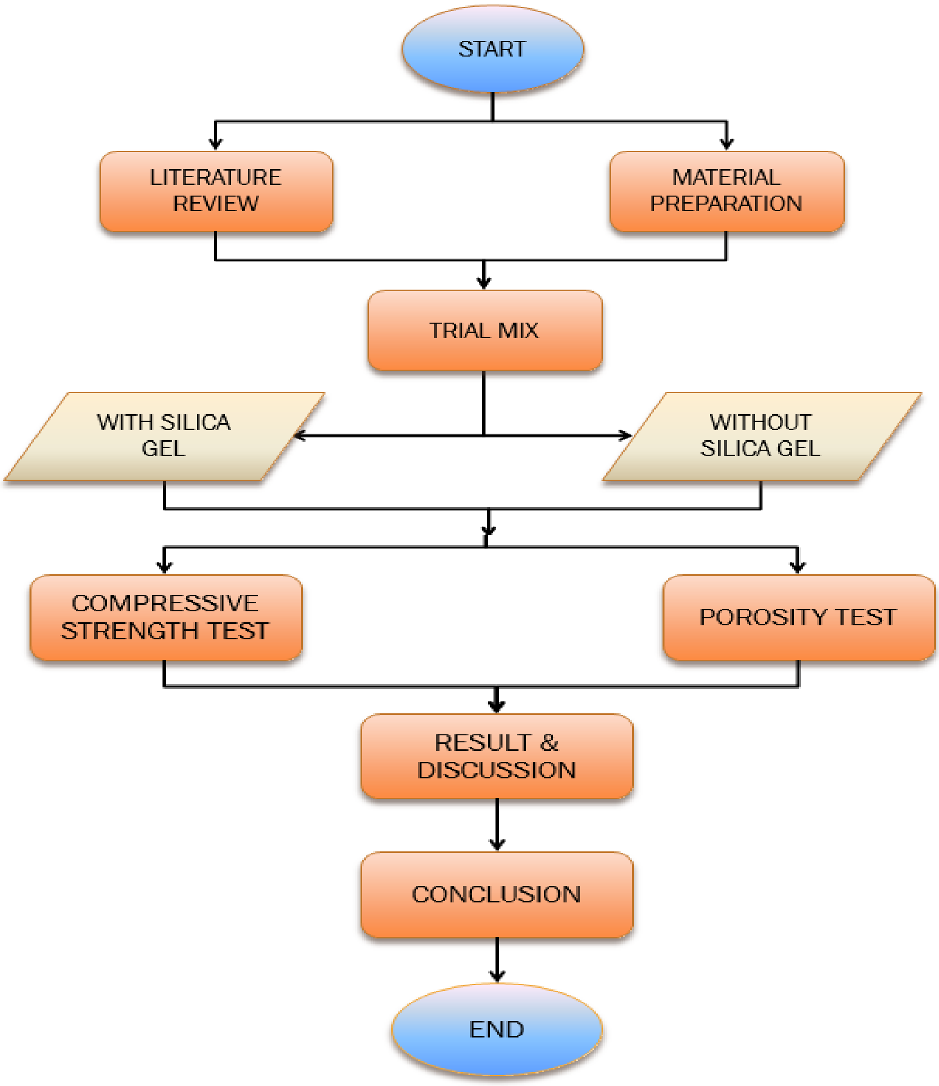

Figure 3.1: Flow Chart of Research Methodology

3.3 MATERIALS

Details of the constituent materials that used to prepare the geopolymer mortar are described in the following sub-chapters. The materials discussed are the main component of geopolymer moratar which include fly ash, sodium silicate solution, fine aggregate as well as the self-healing agent, silica gel.