Influence of TiO_2 and ZnO Photocatalyst onto the Physical, Compressive Strength and Self-Cleaning Properties of Fly Ash-Based Geopolymer Paste

by

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LIST OF ABBREVIATIONS

Ag	Silver
Al	Aluminium
Al_2O_3	Alumina/Aluminium Oxide
BET	Brunaeur-Emmett-Teller
Ca	Calcium
$CaCO_3$	Calcium Carbonate
CaO	Calcium Oxide
$Ca(OH)_2$	Calcium Hydroxide
C-S-H	Calcium Silicate Hydrate
C-A-S-H	Calcium Aluminium Silicate Hydrate
Cr_2O_3	Chromium (III) Oxide
EDX	Energy Dispersive X-ray
FA	Fly Ash
Fe	Ferum/Iron
Fe_2O_3	Hematite/Iron Oxide
Fe_3O_4	Magnetite
FTIR	Fourier-Transform Infrared Spectroscopy
GGBFS	Ground Granulated Blast-Furnace Slag
HA	Hydroxyapatite
HNO_3	Nitric Acid
IR	Infrared
K_2SiO_3	Potassium Silicate
KOH	Potassium Hydroxide
MB	Methylene Blue
MO	Methyl Orange
Na	Sodium/Natrium
NaOH	Sodium Hydroxide
Na_2SiO_3	Sodium Silicate
NO	Nitrogen Oxide
NO_2	Nitrogen Dioxide
NO_3	Nitrates
NO_3^-	Nitrates ion
NOx	Nitrous oxide
O_2	Oxygen
OH^-	Hydroxide Ion

OPC	Ordinary Portland Cement
RhB	Rhodamine B
Si	Silicon
SiO_2	Silicon Dioxide/Silica/Quartz
SEM	Scanning Electron Microscope
Ti	Titanium
TiO_2	Titanium Dioxide/Titania
UV	Ultraviolet
UV-Vis	Ultraviolet-visible Spectroscopy
VOCs	Volatile Organic Compounds
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
ZFAB	Zeolite Fly Ash Bead
Zn	Zinc
ZnO	Zinc Oxide
ZnO_2	Zinc Peroxide
ZrO_2	Zirconium Dioxide

LIST OF SYMBOLS

$\cdot$	Radicals
e-	Electron
h+	Hole
hv	Sunlight/ UV light
$OH^{\cdot}$	Hydroxyl with radical

Pengaruh Fotokatalis TiO_2 dan ZnO terhadap Sifat Fizikal, Kekuatan Mampatan dan Pembersihan-Diri oleh Pes Geopolimer Berasaskan-Abu Terbang

ABSTRAK

Pada masa kini, konsep pembersihan-diri mendapat perhatian yang besar dalam bahan binaan bangunan. Pembersihan-diri dengan kehadiran fotokatalis telah digunakan dalam bahan bangunan untuk mengatasi masalah permukaan bangunan yang cenderung menjadi kotor setelah terdedah untuk masa yang lama di kawasan yang sangat tercemar. Untuk mengikuti konsep bahan campuran persekitaran hijau, terdapat bahan pengikat baru ke arah bahan hijau iaitu geopolimer dengan penambahan fotokatalis telah dihasilkan. Aplikasi pembersihan-diri diperluas dengan menambahkan bahan fotokatalitik nanopartikel ke bahan geopolimer. Walaupun pembersihan diri telah banyak digunakan dalam pes simen konvensional, secara umum aplikasinya dalam geopolimer masih dalam peringkat awal pembangunan yang memerlukan kajian lebih lanjut. Selain kelestarian dari segi penampilan dipertahankan, pengaruh fotokatalis terhadap kemampuan membersihkan diri oleh pes geopolimer yang menawarkan sifat fizikal dan mekanikal yang baik telah difokuskan dalam penyelidikan ini. Pes geopolimer pertama kali disediakan dengan mencampur kering abu terbang dengan pelbagai kandungan nanopartikel (wt%) zink oksida (ZnO) dan titanium dioksida (TiO_2). Nanopartikel ini akan bertindak sebagai fotokatalis untuk mendorong kelakuan pembersihan-diri pes geopolimer. Kemudian, campuran serbuk itu dicampur dengan pengaktif alkali, yang merupakan gabungan larutan natrium hidroksida (NaOH) dengan kepekatan 12M dan larutan natrium silikat (Na_2SiO_3). Nisbah bagi pengaktif alkali, Na_2SiO_3 kepada NaOH ialah 2.5. Sampel telah dibiarkan pada suhu bilik selama 28 hari (awal usia) dan 640 hari (usia matang). Dari analisis komposisi kimia, keputusannya menunjukkan abu terbang sebagai bahan mentah yang digunakan dalam penyelidikan ini mengandungi jumlah kalsium oksida yang rendah (kurang dari 10 wt%), yang dikategorikan di bawah kelas F (kandungan kalsium oksida rendah). Analisis fasa mendedahkan bahawa penambahan nanopartikel ZnO dan TiO_2 tidak mengubah fasa kimia pes geopolimer tetapi telah mempengaruhi sifat mekanik pes geopolimer, di mana kekuatan mampatan berkurangan apabila wt% daripada nanopartikel ZnO dan TiO_2 meningkat. Bukti daripada analisis mikrostruktur menunjukkan keretakan mikro di dalam matrik geopolimer yang disebabkan oleh penggumpalan nanopartikel ZnO yang menyebabkan kekuatan menjadi rendah. Namun begitu, untuk sampel pes TiO_2-geopolimer, dapat diperhatikan bahawa kekuatannya ditingkatkan dari 56 MPa menjadi 86 MPa apabila sejumlah kecil fotokatalis TiO_2 ditambahkan dari 2.5 wt% ke 5.0 wt%. Penambahan nanopartikel ZnO dan TiO_2 juga memberi kesan kepada sifat fizikal (masa pengerasan, keliangan dan penyerapan air) pes geopolimer. Dengan meningkatkan penambahan nanopartikel ZnO dan TiO_2, tempoh pemanjangan masa penetapan meningkat yang menyebabkan masa pengerasan lebih lama. Hasil keliangan menunjukkan bahawa sampel dengan keliangan yang lebih tinggi mempunyai peratusan penyerapan air yang lebih tinggi. Kebolehan pembersihan-diri pes geopolimer telah dinilai melalui ujian aktiviti fotokatalik di bawah cahaya matahari dan cahaya ultraungu (UV) (lampu). Sampel yang mengandungi fotokatalis menunjukkan degradasi metilena biru di mana warnanya berubah daripada biru menjadi tidak berwarna

dari 30 hingga 150 minit terdedah di bawah cahaya matahari dan cahaya UV. Dari analisis UV-Vis, hasilnya menunjukkan bahawa, kadar degradasi meningkat dengan meningkatkan wt% fotokatalis untuk sampel yang dilapisi dan tidak dilapisi dalam kedua-dua keadaan (cahaya matahari dan cahaya UV). Untuk ujian degradasi permukaan, hasilnya menunjukkan bahawa metilena biru terdegradasi sepenuhnya setelah 150 minit terdedah di bawah cahaya matahari dan 600 minit di bawah cahaya UV. Sampel berlapisan juga menunjukkan hasil yang baik untuk degradasi permukaan metilena biru dalam kedua-dua keadaan. Nanopartikel TiO_2 yang mempunyai fotokatalis tertinggi (15.0 wt%) menunjukkan tingkah laku fotokatalitik yang lebih baik dengan kadar degradasi yang lebih tinggi daripada nanopartikel ZnO. Tesis ini menyumbang kepada pembangunan fotokalisis berasaskan pes geopolimer untuk aplikasi pembersihan-diri.

Influence of TiO_2 and ZnO Photocatalyst onto the Physical, Compressive Strength and Self-Cleaning Properties of Fly Ash-Based Geopolymer Paste

ABSTRACT

Nowadays, concepts of self-cleaning have received great attention in construction building materials. Self-cleaning with the presence of photocatalyst was applied in building materials to overcome the problem of surface building tend to become dirty after exposure for a long time in highly polluted areas. In order to pursue the concept of green environment blending materials, a new binding material towards green material which is geopolymer with addition photocatalyst was developed. Although self-cleaning has been widely applied in conventional cement paste, in general their applications in geopolymer are still in early stage of development that requires further study. Besides sustainability in terms of appearances was maintained, the influence of photocatalyst towards self-cleaning ability of geopolymer paste that offer good physical and mechanical properties has been focused on this research. The geopolymer paste was first prepared by dry-mixing of the fly ash with various wt% of zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles. These nanoparticles will act as a photocatalyst to induce the self-cleaning behavior of the geopolymer paste. Then, dry-mixing mixtures were mixed with alkaline activator, which is a combination of sodium hydroxide (NaOH) solution with 12M concentration and sodium silicate (Na_2SiO_3) solution. Ratio of alkaline activator, Na_2SiO_3 to NaOH is 2.5. The samples were cured at room temperature for 28 days (early-age) and 640 days (later-age). From the chemical composition analysis, the result indicates fly ash as a raw material used in this research contain low amounts of calcium oxide (less than 10 wt%), which categorized under Class F (low calcium oxide content) type. Phase analysis revealed that the addition of ZnO and TiO_2 nanoparticles did not change the chemical phase of the geopolymer paste, but did influenced the mechanical properties of the geopolymer paste, where the compressive strength decreased as the wt% of the ZnO and TiO_2 nanoparticles increased. The evidence from microstructure analysis showed microcracks in the geopolymer matrix which caused by agglomeration of ZnO nanoparticles, leads towards low strength. However, for sample TiO_2-geopolymer paste, it can be noticed, the strength was enhanced from 56 MPa to 86 MPa when small amounts of TiO_2 photocatalyst was added from 2.5 wt% to 5.0 wt%. The addition of ZnO and TiO_2 nanoparticles also affect the physical properties (hardening time, porosity and water absorption) of the geopolymer paste. By increasing the addition of ZnO and TiO_2 nanoparticles, prolongation period of setting time was increased that leads longer hardening time. The porosity result demonstrates that sample with higher porosity has higher water absorption percentage. The self-cleaning abilities of the geopolymer paste were evaluated through the photocatalytic activity test and surface degradation test under sunlight and ultraviolet (UV) light (lamp). The sample containing photocatalyst shows degradation of methylene blue where the colour changed from blue to colourless from 30 to 150 minutes under exposure sunlight and UV light. From UV-Vis analysis, the result indicates that, the degradation rate was increased by increasing the wt% of photocatalyst for coated and uncoated sample under both conditions (sunlight and UV light). For surface degradation test, the results show that methylene blue are fully degraded after 150

minutes exposed under sunlight and 600 minutes under UV light. The coated sample also shows excellent results for surface degradation of methylene blue under both conditions. TiO_2 nanoparticles, which have highest photocatalyst (15.0 wt%) shows the better photocatalytic behavior with higher degradation rate than ZnO nanoparticles. This thesis contributed to the development of photocatalyst-based geopolymer paste for self-cleaning application.

CHAPTER 1 : INTRODUCTION

1.1 Research Background

Concrete is one of the most widely used materials in the construction industries (Purushotham, Prasad, & Naveen, 2017). Among others, Portland cement is one of the largest amount of concrete that was utilized as construction materials (Assi, Deaver, Elbatanouny, & Ziehl, 2016). The demand of this type of concrete increases exponentially with the city developments. Besides being used as concrete, cement was also used as a paste for surface finishing of the buildings. However, the high utilization of cement or concrete caused an air pollution, hence give the negative impacts onto the environment (Abdullah, Bnhussain, Hussin, Ismail, & Yahya, 2011). It was known that the production processes of Ordinary Portland Cement (OPC) released high amounts of carbon dioxide (CO_2) to the atmosphere, which in turn has a potential effect on the global warming (Lucas, Ferreira, & Aguiar, 2013).

Due to the high emission of greenhouse gases release during manufacturing of OPC, geopolymer in turn become an alternative material to the OPC by replacing cements-based binder with industrial by-product such as fly ash. Geopolymer is an innovative green construction material that was developed for OPC substitution. It was invented by Davidovits and belong to the family of inorganic polymers (Purushotham et al., 2017). Geopolymer is produced by combining the compound of pozzolanic or aluminosilicate source materials with an alkaline activator solution (Abdullah, Hussin, Bnhussain, Razak, & Yahya, 2012). It can be applied as a paste, mortar or concrete in construction materials. Other than that, it can also be applied commonly in our living surroundings, i.e. paving blocks, exterior tiles and etc. (Guo, Ling, & Poon, 2013).

Fly ash (FA) which is an industrial (coal power plant) by-products, appears to be the most investigating material in the production of the geopolymer due to its physical and morphological properties (Bouaissi, Li, Abdullah, & Bui, 2019). The fly ash also cheap and available worldwide (Aliabdo, Elmoaty, Elmoaty, et al., 2016; Nath, Maitra, Mukherjee, & Kumar, 2016; Rakhimova & Rakhimov, 2019). Thus, it becomes a potential source for the greener production of cements (Rakhimova & Rakhimov, 2019). Instead of using Portland cement, fly based geopolymer paste becoming an alternative because it has the potential to reduce the utilization of Portland cement and at the same time it holds the dominance of Portland cement concrete in terms of physical and mechanical properties (Assi et al., 2016). Geopolymer also was reported to exhibit better compressive strength than OPC concrete (Nath et al., 2016).

In the other hand, in a few years ago, the application of nanoparticles in cement-based materials have attracted much attention due to the unique properties of nanomaterials, which owing to their fine particle size, high reactivity, and specific functional properties. With the implement of nanotechnology in construction and building materials, the performance of concrete based material was improved and enhance in terms of gaining strength, and also new materials development for other functional properties (i.e. self-cleaning properties, discoloration resistance and etc.) (Cohen, Gallego, & Tobon, 2015; Zhang, Cheng, Hou, & Ye, 2015; Ouyang, Han, Cheng, Zhao, & Ou, 2018).

The nanoparticles of photocatalyst (i.e. ZnO and TiO_2) were added in the cementitious material to develop self-cleaning properties. Photocatalyst will decompose of organic and inorganic pollutants to the lesser toxic form under exposure of sunlight and ultraviolet (UV) light. The combination of photocatalyst with cementitious materials has significant advantages. For example, it has the ability in decomposing of the unwanted organic compounds on the surface of the concrete buildings, which easily removed later by the rain (Chen & Poon, 2009; Banerjee et al., 2015; Boonen, Beeldens, Dirkx, & Bams, 2017). As a consequence, building aesthetic appearance is maintained by keeping the surface of the concrete buildings free from dirt and preserves its colour, even in polluted conditions and industrial areas (Khitab, Alam, Riaz, & Rauf, 2014).

However, based on the literature studies, production of the geopolymer with self-cleaning behavior by adding photocatalytic materials such as zinc oxide (ZnO) or titanium dioxide (TiO_2) into the geopolymer materials is not widely explored. Thus, this research aims to investigate the influence of photocatalyst onto the self-cleaning ability of the geopolymer paste while investigating the effect of those particles onto the physical and mechanical behaviour of the products.

1.2 Problem Statement

Nowadays, most of the buildings in Malaysia have low sustainability in terms of the appearance. To be more precise, the concrete of the building, especially the external building walls face the serious problem of tending to become dirty, especially in highly polluted areas for a long-time exposure. Besides that, the demolition of old buildings and natural disasters also contribute to the release of the concrete dust, hence give the dusty and dull in appearances to the surface of the building over the years.

In order to maintain the appearance of the building, the construction industry has focused to produce cementitious materials which not only have a good performance in terms of physical and mechanical, but also has an additional property to clean the surface of building by itself. The self-cleaning concept was applied in conventional cement and have a better performance on physical, mechanical and self-cleaning properties. Meanwhile, in certain cases, the strength was decreased when increase the dosage of addition nanoparticles photocatalyst (Behfarnia, Keivan & Keivan, 2013)

In line to pursue the concept of green environment blending materials, the properties of geopolymer materials was expanded by adding a photocatalyst for self-cleaning purpose. Based on a limited experimental study, there is a lack of studies on the use of geopolymers as self-cleaning materials. There only a few researchers work on geopolymer with addition nanoparticles photocatalyst have already studied, however, only focused on physical and mechanical properties but not discussed about self-cleaning and photocatalytic degradation and etc. Regarding to that, the research aims to study the influence of photocatalytic materials onto physical, mechanical properties and photocatalytic behavior of the self-cleaning geopolymer paste.

1.3 Research Objectives

The main objective of this research is to study the development of fly ash-based geopolymer paste with photocatalytic materials while enhancing physical and mechanical properties for self-cleaning applications. The specific objectives of this research are summarized as follows:

i. To investigate the influence of the photocatalytic materials (ZnO and TiO_2 nanoparticles) onto the physical properties and compressive strength of fly ash-based geopolymer paste.

ii. To evaluate the self-cleaning ability of the photocatalyst-based geopolymer paste through photocatalytic degradation under sunlight and ultraviolet light exposure.

iii. To determine optimum proportion of ZnO and TiO_2 as photocatalyst in fly ash-based geopolymer paste for self-cleaning applications.

1.4 Scope of Research

This scope of the research is focused based on these three main phases. Phase one involved the preparation of the raw materials and the photocatalyst-based geopolymer paste. Fly ash powder and various wt% of ZnO and TiO_2 nanoparticles are dry-mixed prior to mixing with the alkaline activator. The ratio of fly ash to alkaline activator and ratio of sodium silicate to sodium hydroxide will be fixed at 2.0 and 2.5, respectively. Then, the mixtures will be mixed using mechanical mixer and cast in steel mould, follow by curing at room temperature for 28 and 640 days. Three batches of the geopolymer paste are prepared.

In phase two, the physical properties and compressive strength of the prepared geopolymer paste was studied. The physical properties of the geopolymer paste are examined through the setting time, porosity and water absorption test. The mechanical behaviour of the geopolymer paste is determined by the compressive strength test. The physical and mechanical properties of the geopolymer paste with and without the photocatalyst will be evaluated and compared.

Phase three are focused on self-cleaning behaviour observation of the prepared geopolymer paste. Ultraviolet-visible spectrophotometer (UV-Vis) are used to evaluate the self-cleaning abilities of the prepared geopolymer paste through the photocatalytic activity under sunlight and UV light radiation. The degradation rate of methylene blue (MB) solution is measured while the surface degradation of the geopolymer paste is observed. The photocatalytic behaviour of geopolymer paste with and without photocatalyst will be compared.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

This chapter was about review of previous researcher work. There are two main part is described in this chapter. The first part reviews about the cementitious materials, including geopolymer paste and its constituent. It reviews the innovation from conventional cement to the green cementitious materials by using by-product materials. Their mechanism on geopolymerization process and the influence of addition photocatalyst onto physical-mechanical properties toward application geopolymer paste in field work was discussed in detail. The second part reviews on self-cleaning. It reviews the benefit introducing photocatalyst onto cementitious materials, mechanism of photocatalytic reaction, application and utilizing of self-cleaning in cementitious materials and photocatalytic performance in degradation organic and inorganic pollutants.

2.2 Geopolymer

Geopolymer is a new alternative binder to conventional cement as innovation in construction and building materials field, which act as the binder material. The geopolymers properties as a binder that shown in current studies is similar to the OPC binder (Nath, Sarker, & Rangan, 2015; Adak et al., 2017). Joseph Davidovits was a pioneer in introducing geopolymer term in 1979 into an inorganic cementitious area, that represent inorganic polymers. Geopolymer is an eco-friendly construction material that was synthesized from geological materials, since the production of raw materials skip the calcination of limestone which result in low emission of CO_2 that contribute toward sustainability and green environment (Li, Ma, Zhang, & Zheng, 2013; Sahana, 2013; Vora & Dave, 2013; Noushini & Castel, 2016; Adak, Sarkar & Mandal, 2017).

Geopolymer is an inorganic aluminosilicate compound that produced from source material which contains large amounts of silica and alumina react with alkaline activator solutions (i.e. sodium hydroxide (NaOH) or potassium hydroxide (KOH) with sodium silicate (Na_2SiO_3) or potassium silicate (K_2SiO_3), respectively) in order to produced binder, this process is known as geopolymerization (Vora & Dave, 2013; Nath, Sarkar & Rangan, 2015; Aliabdo, Elmoaty, & Salem, 2016; Duan, Yan, Zhou, & Ren, 2016; Noushini & Castel, 2016). Geopolymerization contribute to the minimization of waste technology due to the waste material (e.g. fly ash, slag, kaolin, metakaolin and ground granulated blast-furnace slag (GGBFS)) was used as raw material (Zejak et al., 2013; Aliabdo, Elmoaty & Salem, 2016).

The schematic diagram of geopolymerization process for production fly ash based-geopolymer concrete or cement is shown in Figure 2.1. The mechanism of geopolymerisation process can be explained through these three chemical reaction stages which are (1) dissolution process of Si and Al atoms from the source material by breaking the bond of Si-O-Si and Al-O-Si bond through the hydroxide ions (OH^-) action in alkaline solution and liberation of Al^{3+} and Si^{4+}, leading towards formation of aluminate and silicate monomeric species; (2) Polycondensation or orientation of the Al and Si species in an amorphous three-dimensional aluminosilicate network (gel), which the cations (Si^{4+} and Al^{3+}) are tetrahedrally linked by oxygen bridges; (3) Hardening of aluminosilicate gel into polymeric structures (Shahedan, Abdullah, Hussin, Yahya, Razak & Jamaludin, 2013; Zejak et al., 2013).

Figure 2.1 : Schematic drawings of geopolymerization process for production fly ash-based geopolymer cement/concrete (Zhuang et al., 2016).

As discussed earlier, to be more precise, the main concept behind the mechanism of geopolymer production is the polymerization of the Si-O-Al-O bond which develops when Al and Si that present in source materials (i.e. fly ash) was react with alkali activators solution. In addition, geopolymer also can be exist in the another form by depending upon the Si/Al ratio; (1) -Si-O-Si-O- (poly(silaxo)); (2) -Si-O-Al-O- (poly(sialate)); (3) –Si-O-Al-O-Si-O- (poly(sialate-silaxo)) and (4) –Si-O-Al-O-Si-O-Si-O- (poly(sialate-disilaxo)) (Aliabdo, Elmoaty & Salem, 2016; Noushini & Castel, 2016). Since geopolymer is enriched of Al and Si which originate from fly ash as a source material, the amount of Al and Si in the aluminosilicate gel indicates the level reactivity of fly ash (Abdullah, Hussin, Ismail, BnHussain, Yahya & Razak, 2012). The active cation Al^{3+} and Si^{4+} species was released after aluminosilicate bonds of -Si-O-Si- or -Si-O-Al- was break, then react to form nuclei and aluminosilicate oligomers consists of tetrahedral of $[SiO4]^{4-}$ and $[AlO4]^{5-}$. In aluminosilicate monomers, Si^{4+} is partially substituted by Al^{3+}, and the resultant negative charge in the aluminosilicate chains is balanced by the present of alkali cations (e.g. Na^+ or K^+) in the framework cavities of Al^{3+} in IV-fold coordination (Zejak et al., 2013; Noushini & Castel, 2016; Zhuang et al., 2016).

The fast-chemical reaction of aluminosilicate source and alkali polysilicates between the resultant Si^{4+} and Al^{3+} species through polycondensation, which finally results in the aluminosilicate-based geopolymer formation with three-dimensional aluminosilicate network structure and ring structure which consisting of Si-O-Al-O bonds which has an empirical formula; Mn [-(SiO_2) z-AlO_2] n·w H_2O, where z is the Si/Al molar ratio (i.e. 1, 2 or 3), M is an alkali cation (i.e. Na^+ or K^+), n is the degree of polymerization or polycondensation, and w is the water content (Zejak et al., 2013; Aliabdo, Elmoaty & Salem, 2016; Noushini & Castel, 2016; Zhuang et al., 2016). The main reaction product of geopolymerization is aluminosilicate or geopolymer gel, which is in an amorphous form (Nath, Sarkar & Rangan, 2015). During chemical reaction of geopolymer process, polymerization is a condensation polymerization in which water was released (Aliabdo, Elmoaty & Salem, 2016). The polymerization reactivity reaction of geopolymer was influenced by many factors such as the chemical composition and ratio of mixing binder and alkaline activator solution, condition of curing (including curing period and curing temperature) (Nath, Sarkar & Rangan, 2015; Lee et al., 2017).

2.3 Geopolymer Paste

Geopolymer have been manufactured as paste, mortar and concrete (Li, Ma, Zhang, & Zheng, 2013). For finishing materials, geopolymer paste has been choosen to applied in the outer wall of the building. Geopolymer paste is a hardened cementitious paste which combines waste products into useful product. The reaction between source material that has higher content of silica and alumina with alkaline liquid result to form a geopolymer paste (Li, Ma, Zhang, & Zheng, 2013; Zainal, Hussin, Rahmat, & Abdullah, 2015). For used or testing purpose, the prepared geopolymer paste was cast into a mould and cured at ambient temperature without elevated heat for hardening and geopolymerization process to occur. The development mixtures of geopolymer is suitable for curing at room temperature was extent its application (Nath, Sarker & Rangan, 2015).

However, based on published literature, fly ash is a most commonly choose as a based for geopolymer paste. There is a study on fly ash based geopolymer containing low calcium was cured in ambient temperature (23 °C) without additional heat and the results shows that geopolymer mixtures are suitable for ambient curing due to the condition of the moisture specimens after hardening was improved to be controlled (Duan, Yan, Zhou & Ren, 2016). However, in certain cases, geopolymer paste was cured at required temperature for a specific time in order to be apply in construction materials especially for precast concrete applications (Nath, Sarker & Rangan, 2015; Zhuang et al., 2016; Assi, Ghahari, Deaver, Leaphart, & Ziehl, 2016; Lee et al., 2017) .

Geopolymer paste demonstrate various advantages in terms of properties and characteristics, including sustainable high mechanical strength which gaining in a short time, excellent durability, low shrinkage, high temperature resistance and good in acid resistance which in contrast with OPC (Li, Ma, Zhang, & Zheng, 2013; Sahana, 2013; Duan, Yan, Zhou & Ren, 2016). Geopolymer are ideal for applications in building, repairing infrastructures and also pre-casting due to high early strength properties, remain intact under exposure for a long time and setting time could be controlled (Sahana, 2013). The mechanical strength of geopolymer paste was believed to increase by considering the reaction amounts of combination between SiO_2 and Al_2O_3 in the fly ash. There is an experimental result proved ratio of Si/Al is significantly affected the compressive strength of the geopolymer paste (Lee et al., 2017). Other author reported that, there are others parameter that affecting the compressive strength of geopolymer paste, the ratio of fly ash to alkaline activator (solid-to-liquid ratio) and the ratio of alkaline activator (Na_2SiO_3/NaOH) which had a greater influenced the strength. Thus, the research related to the solid-to-liquid ratio with range of 2.5 to 3.3 and a ratio of sodium silicate to NaOH in the range of 0.4 to 2.5 was investigated, the result demonstrate the optimum solid-to-liquid ratio is 2 while optimum ratio of alkaline activator is 2.5 due to the maximum compressive strength was achieved at this ratio respectively (Abdullah et al., 2012).

The strength development of the geopolymer paste also affected by aluminosilicate or geopolymer gel formation. The existence of the aluminosilicate or the geopolymer gel can be identified in X-ray diffraction (XRD) pattern of geopolymer paste, which is from the broad hump peaks around 20 to 40° of 2 theta with high intensity as shown in Figure 2.2 (Lee et al., 2017). The polymerization reactivity and the strength development of geopolymer paste can be observed through scanning electron microscope (SEM) (Lee et al., 2017). The microstructure of aluminosilicate gel which develops from the solution formed due to partial dissolution of fly ash in alkali solution were undergoing changes due to the Si/Al and Na/Al ratios.

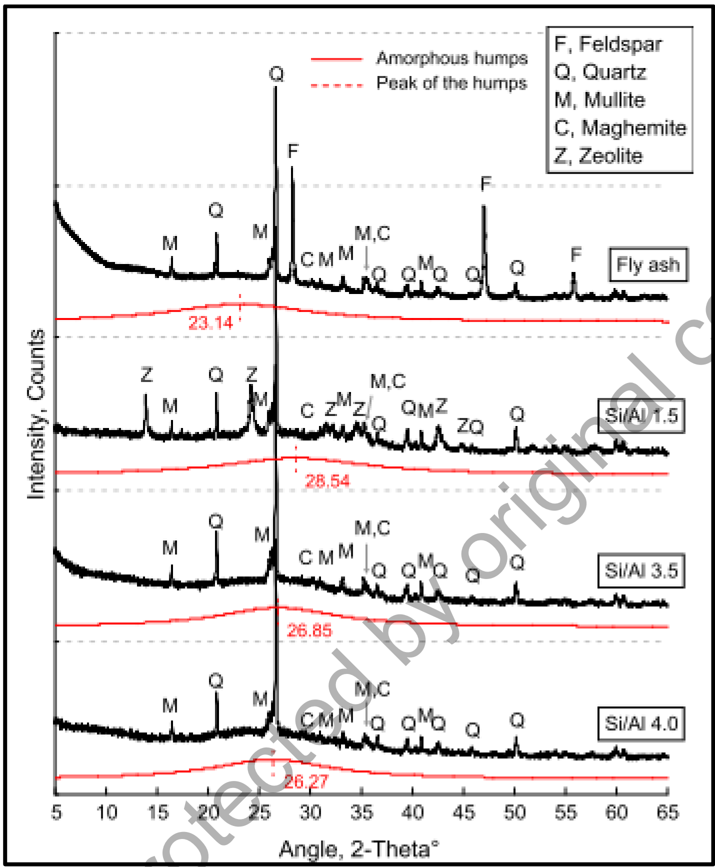

Figure 2.2 : XRD pattern of geopolymer paste (Lee et al., 2017).

SEM result revealed that (as shown in Figure 2.3), the main reaction product in alkali activated fly ash is to form calcium silicate hydrate gel (C-S-H), calcium aluminate hydrate gel (C-A-H), calcium aluminium silicate gel (C-A-S-H) or sodium aluminosilicate hydrate gel (N-A-S-H), (C = CaO, N=Na_2O, A = Al_2O_3, S = SiO_2, H = H_2O) (Bouaissi, Li, Abdullah, & Bui, 2019). Additionally, the fly ash based geopolymer paste has been partially replaced or blended with a small amounts of various additives supplementary cementing materials (e.g. silica fume, metakaolin, rice husk ash and GGBFS) has been studied their effect by several researchers in order to accelerate the reaction at early-age properties and durability performance was enhanced (Sahana, 2013; Nath, Sarker & Rangan, 2015). Nevertheless, there still a few report additions of nanoparticles into geopolymer paste until now.

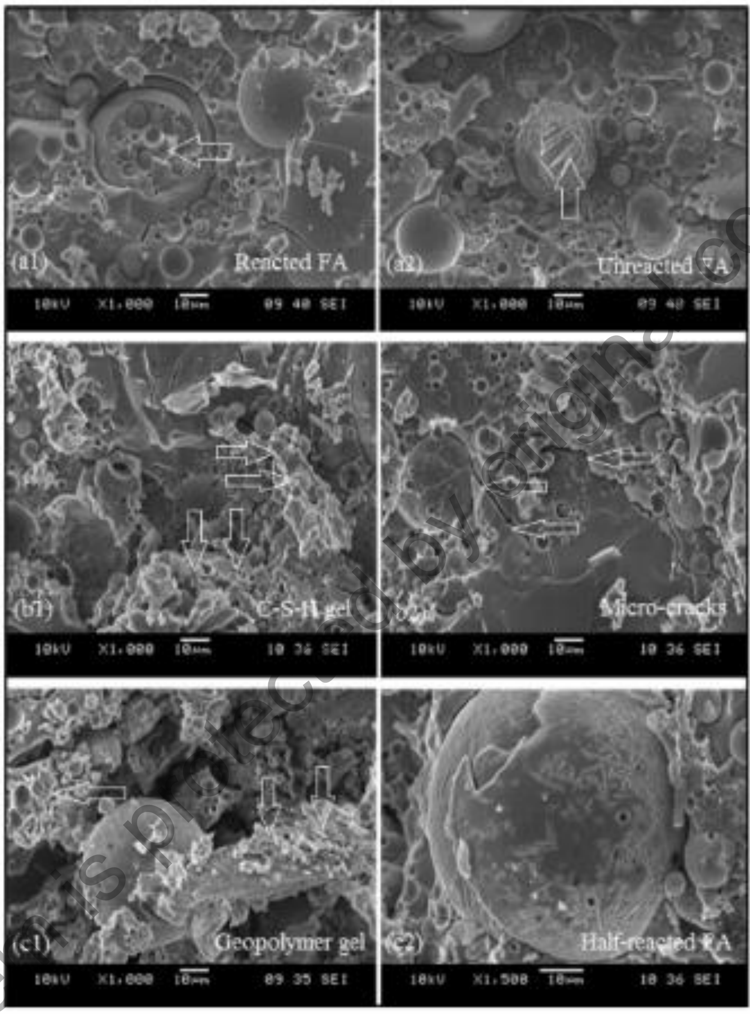

Figure 2.3 : SEM images fly ash-based geopolymer paste (Bouaissi, Li, Abdullah, & Bui, 2019).

2.4 Constituent of Geopolymer Paste

There are two main constituents of geopolymer paste which is source materials and the alkali activator solution. The source materials in geopolymers are based on alumina-silicate materials while solution of alkali activator contains alkali cation which in alkaline solution. Geopolymer paste was produced by waste product as aluminosilicate source materials, which act as binder, react with and was activated by alkaline activator and dissolve in a strong alkaline solution, then reorganize and precipitate in a hardened state. There are some factors that need to be considered in order to choose source materials for making geopolymer, which is cost, availability and type of applications and specific demand of the users (Aliabdo, Elmoaty & Salem, 2016) . However, in certain cases, additive is needed to be added into the geopolymer paste in order to enhance the properties toward specific applications (Kong & Sanjayan, 2010).

2.4.1 Source Materials – Fly Ash

Source materials made of synthesis geopolymer from industrial by products or waste product materials. The source materials act as a binder in geopolymer. In order to produce a geopolymer product, geopolymer source material use aluminosilicate source, which has a high content of silica (Si) and aluminium (Al). The different types of source materials give different performance in geopolymer product. The source materials that mostly be used in the research are fly ash, bottom ash, GGBFS, silico-manganese slag, silica fumes, rice-husk ash, copper and zinc slag, red mud, construction and demolition waste, etc. Other than that, source materials also can be obtained from natural minerals such as clays, kaolinite, metakaolin and etc (Aliabdo, Elmoaty & Salem, 2016; Purushotham, Prasad, & Naveen, 2017). However, among by-product materials, fly ash is the most potential and the most studied materials to replace the OPC as a source material in geopolymer. This is due to the fly ash was available abundantly worldwide raw materials supply from coal-fired electricity generation, low production cost, chemical and mineralogical suitability (Shinde & Kadam, 2013; Nath, Maitra, Mukherjee & Kumar, 2016). FA is the promising materials for cement replacement in terms of low-cost power production and availability huge reserved of good-quality coal worldwide, hence possibility of producing good-quality inorganic binders is higher (Aliabdo, Elmoaty & Salem, 2016; Rakhimova & Rakhimov, 2019; Wattimena, Antoni & Hardjito, 2017).

Fly ash (FA) is a term that used to describe any fine particulate material precipitated in industrial furnace. Fly ash is an industrial by-product material which derived from combustion of coal which has high amount of silica (SiO_2) and alumina (Al_2O_3) that require a highly concentrated alkaline solution in order to develop inorganic aluminosilicate gel. FA is a new technology in construction materials that contained high silica and alumina and have great potential as one of the main sources of aluminosilicate materials for geopolymer binder. FA rich aluminosilicate source materials that applicable for utilization as a raw material in industries and construction materials due to the improving their physical and mechanical properties (Wattimena, Antoni & Hardjito, 2017). In the other hand, the fly ash are also known as pozzolanic material that incorporated substitution partially in cement with the moisture presence and chemically react at an ordinary temperature in order to form compounds possessing cementitious properties (Wattimena, Antoni & Hardjito, 2017).

Fly ash based geopolymer as a cement binder replacement was successfully applied in civil engineering (Zejak, Nikoli, Blecic Radmilovic, & Radmilovi, 2013). The suitability of the FA to be utilized in cementitious materials is determined by its physical features, phase and chemical composition. In terms of physical features, FA is suitable for use in geopolymer due to the spherical shape that being observed through morphology studies which is good in bonding during geopolymerisation (Ryu, Lee, Koh, & Chung, 2013). In terms of phase composition, fly ash are well-known as oxide-rich materials due to FA consist varying amount of mineral which has crystalline phase such as quartz (SiO_2), mullite ($3Al_2O_3SiO_2$), hematite (Fe_2O_3) and magnetite (Fe_3O_4) that determined through mineralogical determination. These crystalline phases are essentially inert in concrete and in order cementitious hydrates to form, a source of alkali or lime (i.e. $Ca(OH)_2$) are required by the glass for reaction (Thomas, 2007; Duan, Yan, Zhou & Ren, 2016; Ghazali, Muthusamy & Ahmad, 2019). The raw materials that have been used contain high content in Silicon (Si), Alumininium (Al), Calcium (Ca) and Ferum (Fe) which indicates the performance of geopolymer materials are good enough to be applied as cementitious materials (Abdullah, Hussin, Bnhussain, Ismail & Ibrahim, 2013; Duan, Yan, Luo, & Zhou, 2016). There is an author reported that, the reactivity of fly ash was enhanced to improve by increasing the fineness (Nath, Sarker & Rangan, 2015).

From chemical composition aspect, FA is classified based on the type of coal from which the ash was derived. American Society for Testing and Materials (ASTM) C618 − 12a is the benchmarks characterization and classification of fly ash which are broadly classified worldwide into three classes, i.e. class F, class C and class N (Bhatt et al., 2019). The major differences among these three classes is due to the different amount of calcium, alumina, silica and iron content in chemical composition. This is due to the fly ash typically contains significant amount of silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3) and calcium oxide (CaO). In the other hand, fly ash also are categorized based on the chemical composition requirements, when total composition of reactive oxide (SiO_2+Al_2O_3+Fe_2O_3) are more than 70 wt%, FA are defined as class F (low calcium fly ash) which is pozzolanic in nature that contain less than 10 % of lime (CaO) content. Meanwhile, if the SiO_2+Al_2O_3+Fe_2O_3 content between 50 and 70 wt%, FA are defined as class C (high calcium fly ash) which has both pozzolanic and cementitious properties and contain more than 10 % CaO content. Meanwhile, class N is made up from natural pozzolan (Akhtar & Tarannum, 2016; Bhatt et al., 2019; Ghazali, Muthusamy & Ahmad, 2019).

A low calcium fly ash utilized as binder in construction materials because of the microstructure and geopolymerization process was altered with the presence high amount of calcium (Lloyd & Rangan, 2010; Wattimena, Antoni & Hardjito, 2017). An alkaline solution activated the low calcium fly ash for production of geopolymer. Low calcium fly ash is normally chosen as the main source materials due to it has better capability to increase the resistance to sulphate attack and heat of hydration of concrete was reduced (Gamage, Liyanage, Framogeni & Setunge, 2011). In previous studies, the researchers are generally focused on low calcium fly ash due to amount of calcium has significant influence the mechanical properties (Li, Ma, Zhang & Zheng, 2013). This indicated that the calcium content in fly ash plays a significant role in the development of strength. Low calcium fly ash extends both the initial and final setting time which result in late hardening and influence the physical and mechanical properties. Meanwhile, high calcium fly ash is rapid harden in setting time due to the its unique self-hardening characteristics and self-cementing properties which not require an activator unlike Class F (Thomas, 2007; Akhtar & Tarannum, 2016).

Fly ash has been utilized in many different ways in manufacturing building materials, for instance, bricks, concrete, lightweight aggregate and cement-composites such as slabs, beams, columns, wall panels, sheets, pipes, etc. Other than that, fly ash is used as a material for road construction and earth filled dam construction (Gamage, Liyanage, Framogeni & Setunge, 2011; Ghazali, Muthusamy & Ahmad, 2019; Wattimena, Antoni & Hardjito, 2017). There is an author recommended class F fly ash to be utilized as filling material in construction field (i.e., building, roads, embankments, low lying areas) (Akhtar & Tarannum, 2016). Thus, it can be concluded that fly ash class F type is suitable for the production of building materials and structural applications.

2.4.2 Alkaline Activator

Alkaline activator solution plays an important role in geopolymerization. Davidovits proposed that geopolymerization process occur when an alkaline liquid was used to react with the Si and Al in a source material which is from geological origin in order to produce binders, the geopolymer term was introduced to represent these binders (Lloyd & Rangan, 2010). The alkali activation of waste materials is a chemical process transforming glassy structures (partially or totally amorphous and or metastable) into very compact well-cemented composites (Duan, Yan, Zhou & Ren, 2016). The soluble alkali metals such as sodium (Na) or potassium (K) based usually to be used as alkaline liquids and this alkali cations (i.e. Na^+ or K^+) balanced the resultant negative charge in the aluminosilicate chains along with the process of geopolymerization (Yu et al., 2016). The alkaline activator that frequently used is a combination of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) or potassium hydroxide (KOH) and potassium silicate (K_2SiO_3), respectively (Lloyd & Rangan, 2010; Purushotham, Prasad & Naveen, 2017).

However, the combination of sodium silicate and sodium hydroxide solution is the more preferred activating solution that was utilized in research studies (Assi et. al, 2016). This is because the addition of Na_2SiO_3 solution to the NaOH solution as the alkaline activator enhanced the reaction between the source material and the solution that used to activate the source material which resulted in a higher strength (Budh & Warhade, 2014). The same idea was discussed by Yu et al., (2016), sodium silicate solution combined with NaOH is to increase strength due to the high viscosity of Na_2SiO_3 was assist the geopolymer gels formation and produce dense microstructure of fly ash-based geopolymer (Yu et al., 2016).

In the other hand, the concentration of NaOH also contributes to the development strength of geopolymer paste, whereas NaOH concentration solution within the range of 8 to 16 M are recommended to be used (Abdullah et al., 2012). The increase in molarity of sodium hydroxide in alkaline solution results in increase the compressive strength of the geopolymer paste (Budh & Warhade, 2014). The higher concentration of sodium hydroxide results in the more dissolution of the fly ash, thus increase the degree of geopolymerization (Li, Ma, Zhang & Zheng, 2013). The recommended range due to the previous researchers had conducted the experiment and the result shows that the compressive strength of a geopolymer paste was increased as the concentration of NaOH increases from 4.5 to 14 M, meanwhile, at 16.5 M of NaOH concentration, the compressive strength of a geopolymer paste was decreased (Lee et al., 2017). Fly ash-based geopolymer resulted in high compressive strength with 12 M sodium hydroxide concentrations. Abdullah, Hussin, Bnhussain, Razak, & Yahya (2012) reported that 12 M concentration of NaOH was contributed to the highest compressive strength compared to the 6 and 10 M solutions. The optimum of NaOH concentration is 12 M was discovered by many authors at which geopolymer exhibits the best mechanical properties at this concentration and indicates a better result than other concentration (Abdullah et al., 2011; Abdullah et al., 2012; Abdullah et al., 2012; Hamidi, Man & Azizli, 2016).

Otherwise, the ratio of fly ash to alkaline activator (solid-to-liquid ratio) also influences the compressive strength of the fly ash-based geopolymer. The compressive strength increase with increasing solid-to-liquid ratio (Abdullah et al., 2011). A ratio of sodium silicate to NaOH in the range of 0.4 to 2.5 was investigated, the result demonstrates the geopolymer paste with a combination of sodium silicate and sodium hydroxide (12 M) with solid-to-liquid ratio 2 while optimum ratio of alkaline activator is 2.5 due to the highest compressive strength was achieved at this ratio (Abdullah et al., 2012; Abdullah et al., 2012).

2.5 Self-Cleaning

2.6 Self-Cleaning Mechanism

Self-cleaning is an automatic cleaning process. In 1973, the principle of self-cleaning was discovered by the botanist Wilhelm Barthlott (Banerjee, Dionysiou, & Pillai, 2015). This is due to its photocatalytic action on the pollutants which removed with the addition of titanium dioxide as photocatalyst (Vignesh, Sumathi, & Mohan, 2018). The properties of self-cleaning is a "bio-inspired" materials that mimic biological systems which exhibit the "lotus effect". The surface exhibiting the lotus effect was created due to the functionalized nanoparticles, such as SiO_2, TiO_2, ZnO, calcium carbonate ($CaCO_3$) or hydroxyapatite (HA) (Alfieri et al., 2017).

Self-cleaning has an ability to clean their surfaces by itself. Self-cleaning is widely used in cementitious materials because it improves the mechanical properties and performance due to its properties. The advance in photocatalytic materials research has established a solid foundation for its extended applications in the field of construction and building materials (Chen, Kou, & Poon, 2012). Photocatalytic reaction uses the energy from ultraviolet rays to oxidize organic compounds and able to degrade the other pollutants to a lesser toxic form under exposure to sunlight. Photocatalytic reaction occurs with the presence of ultraviolet (UV) radiation from the sun. When light and heat strike the surface of concrete which are covered by a layer of photocatalytic materials, photocatalyst use the energy to disintegrates the organic pollutant into the oxygen, water, nitrate, sulphate molecule, CO_2 and etc., as shown in Figure 2.4 (Boonen & Beeldens, 2005; Kumar, Srivastava, & Bansal, 2013; Patil & Pendharkar, 2016; Vignesh, Sumathi & Mohan, 2018)

The products from the reaction of self-cleaning are easily removed by rain or simple rinsing due to the superhydrophilic surface which is nature from photocatalyst (Banerjee, Dionysiou & Pillai, 2015). The photocatalytic components consume the energy from sunlight to oxidize organic and inorganic compounds. Air pollutants that causes discoloration to the exposed surfaces are removed and their residues are washed off by rain. Thus, this is an innovation to minimize the maintenance costs while ensure a cleaner environment (Barbesta & Schaffer, 2009).

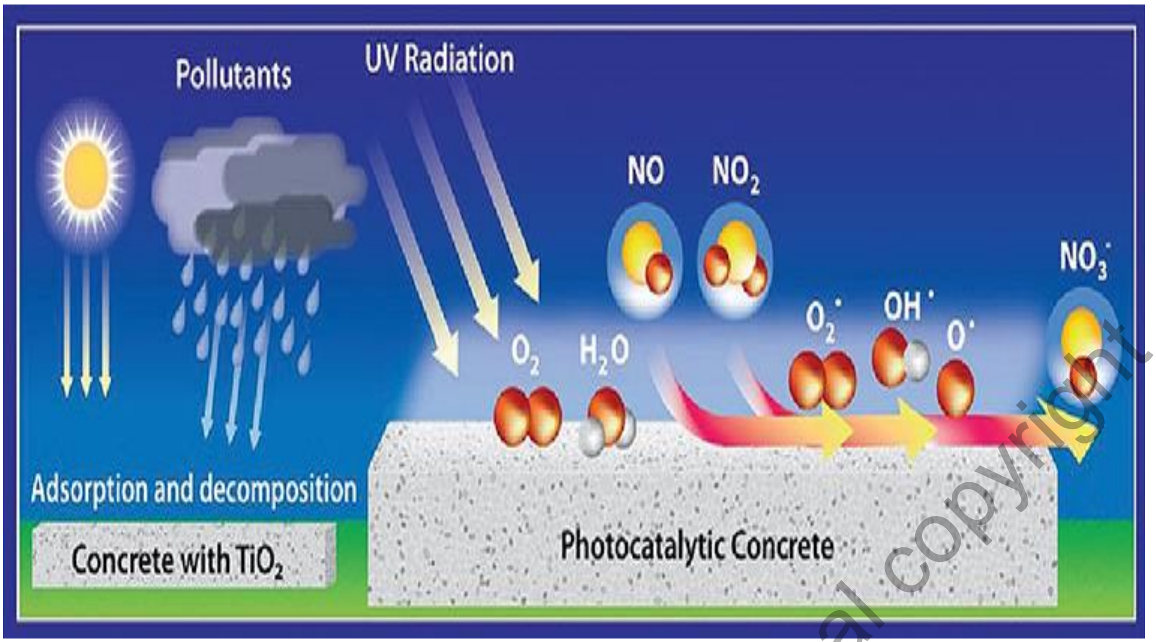

Figure 2.4 : Mechanism of self-cleaning on surface of cementitious materials (Boonen & Beeldens, 2013).

Other than that, photocatalyst convert organic particles and air pollutants that contain toxic to lesser toxic forms in the presence of UV radiation from the sun, e.g. nitrogen oxides (NOx, NO + NO_2) decomposed into lesser toxic which is nitrogen dioxide (NO_2), nitrate (NO_3), etc. In photocatalytic reaction, NOx gases were first break down into nitric acid (HNO_3) and attach to the water droplet. Then, the water droplet is then be washed away by rain, then due to the photocatalytic effect, nitric oxide (NO) was oxidised and become nitrates ion (NO_3^-) and was flushed from the surface as a weak HNO_3 as illustrated in Figure 2.5. This is a promising approach for self-cleaning surfaces and at the same time, air pollution which is the main environmental problem was solved by NOx degradation (Dolatabadi, 2013; Shen et al., 2015). This same photocatalytic reaction also contributes to the decomposition of volatile organic compounds (VOCs), as consequent, contaminants and impurities are removed from the surrounding environment (Vignesh, Sumathi & Mohan, 2018).

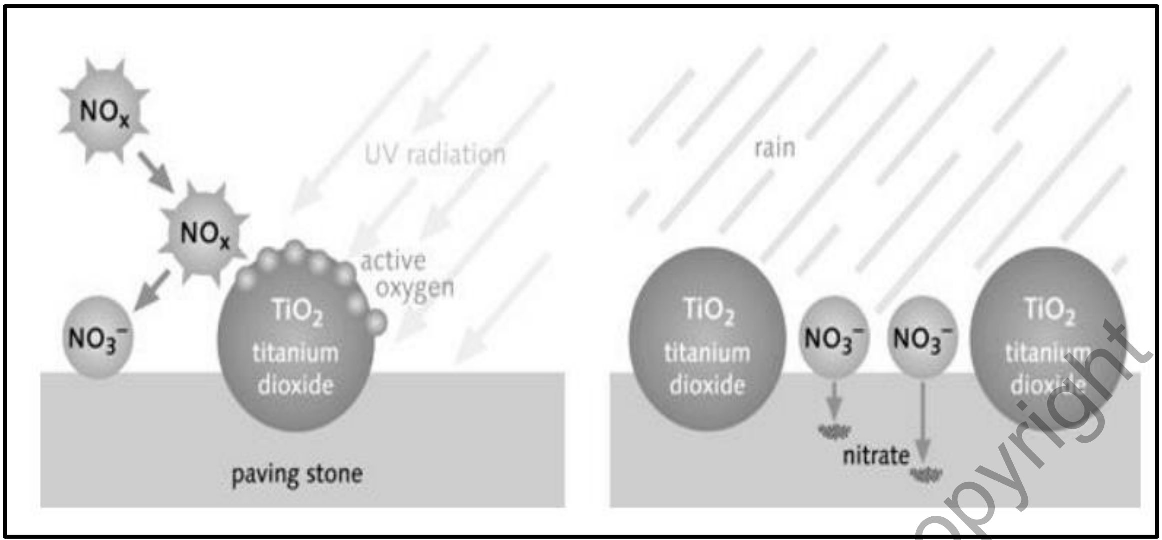

Figure 2.5 : Photocatalytic reaction process of cementitious materials (Dolatabadi, 2013).

The building can maintain their aesthetical appearance by avoiding the dirt and stains to stay attached to the building surface and improve the quality of air by the degradation of airborne pollutants (Cardenas, Tobon, Garcia & Vila, 2012; Smits et al., 2013). Thus, the application of photocatalyst was highlighted to achieve eco-friendly and sustainable concrete which greatly help to lower production and ecological cost of construction materials (Jibhenkar, Vaidya, Waghmare & Singh, 2015).

2.7 Self-Cleaning Technology

Self-cleaning technology is commercialized for indoor and outdoor applications. In the last few decades, indoor and outdoor pollution has become a significant concern due to the exponential growth in the urbanization and industrialization over the world (Ratan & Saini, 2019). In world nowadays, there are limitless technologies existing that has derived from nature, which is technology of self-cleaning is one amongst them. There are various applications of self-cleaning technology in practically such as car mirror, solar