THE ROLE OF ALKALINE ACTIVATOR IN GEOPOLYMERIZATION OF LOW-CALCIUM FLY ASH BASED GEOPOLYMERS.

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بسم الله الرحمن الرحيم

In The Name of Allah The Most Gracious and The Most Merciful.

With The Selawat and Salam to Prophet Mohammad SAW.

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DECLARATION OF THESIS

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Peranan pengaktif beralkali dalam proses pengeopolimeran bagi fly ash rendah kalsium berasaskan geopolymer

ABSTRAK

Polimer bukan organik atau geopolimer ringkas telah disintesis dalam kajian ini dengan pemangkin beralkali dari sisa abu pembakaran berkalsium rendah tempatan (Kelas F). Cecair pemangkin beralkali yang digunakan untuk proses pengaktifkan adalah campuran silikat sodium (waterglass) dan larutan natrium hidroksida (NaOH). Tujuan utama kajian ini adalah untuk mengkaji kesan kandungan dan unsur nisbah campuran pemangkin beralkali (silikat sodium dan larutan NaOH) pada kekuatan mampatan dan stuktur mikro hasil daripada geopolimer berkalsium rendah berasaskan sisa abu pembakaran. Geopolimer disediakan pada parameter operasi tetap, yang meliputi: kosentrasi larutan NaOH (15M), air tambahan (17% daripada berat geopolimer), masa campuran (15 minit), masa pengembangan (24 jam), suhu curing (70° C), masa curing (24 jam) dan masa penuaan (24 jam). Kandungan pemangkin beralkali diverifikasi berdasarkan nisbah jisim Pemangkin/Sisa abu pembakaran digunakan di dalam kajian masa ini, iaitu (0.3, 0.35 dan 0.4), dan nisbah unsur campuran pemangkin beralkali atau nisbah silikat sodium/NaOH (0.6, 0.8, 1.0 and 1.2) disahkan. Kekuatan tekanan yang tertinggi dikekalkan pada kandungan pemangkin beralkali (Pemangkin/Sisa abu pembakaran = 0.4). Kekuatan mampatan dan data SEM menunujukkan bahawa bagi setiap nisbah Pemangkin/Sisa abu pembakaran (0.3, 0.35 dan 0.4), nisbah optimum silikat sodium/NaOH (masing-masing 0.8, 1.0 dan 1.0); memberikan kekuatan mampatan dan keseragaman paling tinggi, pengurangan liang pada struktur mikro dengan pengurangan tindak balas pada sisa abu pembakaran. Analisa XRD menunjukkan pembentukkan geopolimer pada nisbah optimum silikat sodium/NaOH terutama amorphous dengan kewujudan fasa penghabluran yang sedia ada di dalam sisa abu pembakaran dan sesetengah fasa zeolatik yang terbentuk semasa proses geopolimer. Kekuatan mampatan geopolimer optimum (8.61 Mpa, nisbah Pengaktif/Sisa abu pembakaran = 0.4 dan silikat sodium/NaOH = 1.0), menunjukkan kebolehan terma yang rendah pada 400° C, berdasarkan formasi daripada keretakan makro pada permukaan sampel yang disebabkan oleh pengewapan air dan kemerosotan akan berlaku serta proses pesinteran berlangsung pada suhu yang lebih tinggi iaitu 600°C dan 800°C.

The role of alkaline activator in geopolymerization process of Low-calcium fly ash based geopolymers.

ABSTRACT

Inorganic polymers or simply geopolymers were synthesized in this study by the alkaline activation of local low-calcium (Class F) fly ash. The alkaline activator liquid used for the activation process was a mixture of sodium silicate (waterglass) and sodium hydroxide (NaOH) solution. The main purpose of the research was to study the effect of the alkaline activator content and the alkaline activator constituents (Waterglass and NaOH solution) mixing ratio, on the compressive strength and on the microstructure of the resulted low-calcium (Class F) Fly ash-based geopolymer. The geopolymers were prepared at fixed operation parameters, which were including: the concentration of NaOH solution (15M), additional water (17% of the geopolymer weight), mixing time (15min), dilation time (24hr), curing temperature (70°C), curing time (24hr), and aging time of (24hr). The alkaline activator content was verified according to the Activator/Fly ash mass ratios utilized in the current research, which were (0.3, 0.35, and 0.4), and verified the mixing ratios of the alkaline activator constituents or waterglass/NaOH ratios were (0.6, 0.8, 1.00, and 1.2). The highest compressive strength was obtained at highest alkaline activator content (Activator/Fly ash =0.4). The compressive strength and the SEM data also showed that for each Activator/Fly ash ratio (0.3, 0.35, and 0.4), an optimum waterglass/NaOH ratio of (0.8, 1.00, and 1.00 respectively); give the highest compressive strength and a homogenous, less porosity microstructure with less unreacted fly ash spheres. XRD analysis showed that the formed geopolymers at the optimum waterglass/NaOH ratios were mainly amorphous with presence of crystalline phases existed in the original fly ash and some zeolitic phases were formed during the geopolymerization process. The optimum compressive strength geopolymer (8.61 MPa, Activator/Fly ash ratio = 0.4, and waterglass/NaOH =1.00), shows low thermal durability at 400°C, by the formation of macrocracks on the sample surface due to the water evaporation and further deterioration and sintering process takes place at higher temperatures of 600 & 800°C.

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LIST OF SYMBOLS, ABBREVIATIONS OR NUMENCLATURE

OPC	Ordinary Portland Cement
Si	Silicon
Al	Aluminum
O	Oxygen
Na	Sodium
K	Potassium
Ca	Calcium
Mg	Magnesium
M^+	Alkali Ion
CO_2	Carbon dioxide
CaO	Calcium Oxide
H_2O	Water
Na_2O	Sodium Oxide
Al_2O_3	Aluminum Oxide
SiO_2	Silicon Oxide
Fe_2O_3	Iron Oxide
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
Waterglass	Sodium Silicate Solution
Class F	Low-calcium Fly ash
Class C	High-calcium Fly ash
XRD	X-ray Diffraction
ACI	American Concrete Institute
LOI	Loss On Ignition
%	Weight percent
SEM	Scanning Electron Microscopy
m	Meter
Al-Si	Aluminosilicate
M	Molar
MPa.	Mega Pascal
θ	Theta

RT	Room Temperature
PSS	Polymer(sialate-siloxo)
cP	Centipoise
cc	Centimeter Cubic
gm	Gram
hr	Hour
°C	Degree Celsius
min	Minute
mm	Millimeter
ASTM	American Standard Testing Material
KN	Kilo Newton
kV	Kilo Volt
Å	Angstrom
S	Second
Mam	Milliampere
µm	micrometer

CHAPTER 1

INTRODUCTION

1.1 Background

Concrete usage around the world is second only to water. Ordinary Portland cement (OPC) is conventionally used as the primary binder to produce concrete. The environmental issues associated with the production of OPC are well known (Hardjito et al., 2005). The amount of carbon dioxide released during the manufacture of OPC due to the calcination of limestone and combustion of fossil fuel is in the order of one ton for every ton of OPC production. In additional, the extent of energy required to produce OPC is only next to steel and aluminum.

As early as the 1980s Davidovits proposed a controversial theory that some of the Pyramids in Egypt were not built by mining limestone blocks and moving them into place but were cast in place and allowed to set, creating an artificial zeolitic rock. This theory, which gained acceptance, culminated in a book *"The Pyramids An Enigma Solved"*, written together with Magie Morris and published in 1988. Intensive research, initiated by Davidovits and co-workers, to prove this theory has resulted in the rediscovery of a new family of mineral polymers, which they called *alkali -activated aluminosilicate geopolymer* or simply *geopolymers.* This name was chosen because of the similarities with organic condensation polymers in regards to their hydrothermal synthesis conditions (Davidovits, 1982; Davidovits & Sawyer, 1985; Davidovits, 1988; Davidovits, 1994a).

Over the last twenty years, geopolymer also known as *mineral polymer* or *inorganic polymer glasses,* have received much attention as a promising new form of inorganic polymer material that could substantially substitute for conventional or ordinary Portland cement, plastics and many mineral-based products. However, to date the exact mechanisms that cavern geopolymerization are still not fully understood (Hardjito et al., 2005).

Geopolymers are members of the family of inorganic polymers. The chemical composition of the geopolymer material is similar to natural zeolitic materials, but the microstructure is amorphous. Zeolites composition is based on aluminosilicate framework and three dimensional network inorganic polymers built up of (Si, Al) O_4 tetrahedra linked by sharing oxygen atoms into rings and cages. The polymerization process (geopolymerization) involves a substantially fast chemical reaction under alkaline condition on Si-Al minerals that result in a three dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds (Davidovits, 1994a).

Moreover, as the geopolymers synthesizing technology is basing on the alkaline activation of source materials contains mostly Silicon (Si) and Aluminum (Al) in amorphous form (Hardjito et al., 2004), the similarity of some fly ashes to natural aluminosilicates (due to the presence of SiO_2 and Al_2O_3 in the ash) has encouraged the use of geopolymerization as a possible technology solution in the making of special cement (Silvestrim et al., 1997, 1999). The successful stabilization and immobilization of some toxic heavy metals in geopolymeric material by Jaarsveld et al. (1998), Jaarsveld & Deventer (1999), has also encouraged the use of this fairly new technology.

1.2 Problem Statement

Most researches done on the fly ash-based geopolymers were focusing on the manufacturing of fly ash-based geopolymers, and study the operation parameters influencing on the mechanical properties of the resulted concrete like mixing time, NaOH solution concentration, curing temperatures, curing time, aging conditions, chemical resistance property, aggregate materials content, and the Microstructure characterization of the produced geopolymer at range of Activator/Fly ash ratios 0.25 to 0.45(Palomo et al., 1999a; Jaarsveld et al, 1998; Jaarsveld & Deventer, 1999; Xu & Deventer, 2000; Bakharev, 2005; Hardjito & Rangan, 2005 and Fernandez-Jimenez & Palomo, 2003). These others used low-calcium (Class F) fly ash as based materials for making geopolymers. The alkaline activator used in the activation process was mixture of sodium waterglass and NaOH solution mixed at constant waterglass/NaOH. However, very little was available in the published literature regarding to the effect of the waterglass/NaOH mass ratio on the mechanical compressive strength and microstructure of low-calcium (Class F) fly ash-based geopolymer.

Whereas, Chindaprasirt et al. (2007), reported the effect of the mass mixing ratio of waterglass/NaOH, on the workability and compressive strength of geopolymers synthesized using high-calcium (Class C) fly ash. They used range of waterglass/NaOH ratios of 0.67, 1.00, 1.5, and 3.0.

This research was therefore dedicated on study the role of the alkaline activator (waterglass + NaOH solution) content and mixing procedure on the mechanical compressive strength and microstructure properties of low-calcium fly ash based geopolymers synthesized at different Activator/Fly ash ratios.

1.3 The Geopolymerization Mechanism

The exact reaction mechanism which explains the setting and the hardening of alkali-activated geopolymers is not yet quit understood, although it is thought to be depended on the prime material as well as on the alkali activator. According to Glukhovsky et al. (1980), the mechanism of alkali- activation is composed of conjoined reactions of destruction-condensation ,that include the destruction of the prime material in to low stable structural units ,their interaction with coagulation structures and creation of condensation structures . The first steps consist of breakdown of covalent bounds Si-O-Si and Al-O-Si, which happened when the PH of the alkali solution rises, so those groups are transformed in a colloid phase. Then an accumulation of the destroyed products occurs, which interacts among them to form a coagulated structure, leading in a third phase to the generation of a condensed structure.

However, Zuhua et al. (2009) reported that the geopolymerization process occurred approximately into two periods: the dissolution- hydrolysis period and the hydrolysis-polycondensation period. But the fact, these two steps probably occur simultaneously once the solid material mixed with the alkaline activator (Hongling & Deventer, 2003). The exact separation of these two steps is hard and the partition here is only from the point of view of thermodynamics, the period (I) including the dissolution of the SiO_2 and Al_2O_3 species and hydrolyses it, as indicated in the equations (1.1) to (1.3), (Zuhua et al., 2009).

$$-Si-O-Si- + H_2O \xrightarrow{OH^-} 2-Si-OH \qquad (Eq.1.1)$$

$$-Al-O-Al- + H_2O \xrightarrow{OH^-} 2-Al-OH \qquad (Eq.1.2)$$

$$-Si-O-Al- + H_2O \xrightarrow{OH^-} -Si-OH + -Al-OH \qquad (Eq.1.3)$$

$$-Si-OH + -Al-OH \xrightarrow{OH^-} HO-\underset{/\;OH}{\overset{OH\;/}{Si}}-O-\underset{/\;OH}{\overset{OH\;/}{Al}}-OH + H_2O \qquad (Eq.1.4)$$

$$n\,(OH)_3-Si-O-Al(OH)_3 \xrightarrow{NaOH} Na^+ \ldots .(\underset{/}{\overset{/}{Si}}-O-\underset{/}{\overset{/}{Al}}-O)n + 3n\,H_2O \qquad (Eq.1.5)$$

$$n(OH)_3-\underset{/}{\overset{/}{Si}}-O-\underset{/\;OH}{\overset{OH\;/}{Al}}-O-Si-(OH)_3 \xrightarrow{NaOH} Na^+ \ldots(-O-\underset{/}{\overset{/}{Si}}-O-\underset{/\;OH}{\overset{OH\;/}{Al}}-O-Si-)n + 3nH_2O \qquad (Eq.1.6)$$

The water is the reactant in this period, if the (OH^-) concentration is high enough; more water will accelerate the dissolution and hydrolysis period. In the meantime, the water plays as product in the period (II), as indicated in equations (1.4) to (1.6). If the water content is too much, will hinder the geopolymerization kinetically (Zuhua et al., 2009).

1.4 Low-calcium (Class F) Fly Ash Based Geopolymer

In this research, the Low-calcium (Class F) fly ash is used as binder, instead of OPC or any hydraulic cement paste. The alkaline activator used for activated the fly ash, was a mixture of sodium waterglass and sodium hydroxide solution NaOH. The preparation procedure was aiming to verify the alkaline activator content as well as the mixing procedure of the activator liquid constituents, in order to investigate the influence of the changing parameters on the mechanical compressive strength and the microstructure of the prepared geopolymers. Therefore, the operation parameters including (NaOH solution concentration, mixing time, dilation time, curing temperature, curing time, and aging period) were fixed during the preparation processes. And no aggregate materials or admixtures were used in the preparation process. The geopolymers materials were prepared at Activator/Fly ash ratios of (0.3, 0.35, and 0.4) following the recommended range of Activator/Fly ash ratios (0.3-0.45), suggested by Rangan (2008).

1.5 Objectives Of The Research

This research have been done in order to investigate the effect of the alkaline activator content and mixing procedure on the mechanical compressive strength and the microstructure of low-calcium (Class F) fly ash based geopolymers. Regarding to this scope the following objectives has been taken for this research:

1. To identify the effect of Activator/Fly ash ratio on the workability of fresh paste and on the mechanical compressive strength of the hardened low-calcium (Class F) fly ash based geopolymer.
2. To study the effect of alkaline activators (waterglass/NaOH) mass ratio on the compressive strength and the microstructure of low-calcium (Class F) fly ash