



**EFFECT OF MIXING CONDITIONS ON
THE PROPERTIES AND
CHARACTERISTIC OF KAOLIN
GEOPOLYMERS**

by

**HEAH CHENG YONG
(1040410479)**

A thesis submitted in fulfillment of the requirements for the
degree of Doctor of Philosophy

**School of Materials Engineering
UNIVERSITI MALAYSIA PERLIS**

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LIST OF ABBREVIATIONS

aq	Aqueous
BET	Branauer-Emmett-Teller
CO ₂	Carbon Dioxide
CSH	Calcium Silicate Hydrated
EDX	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
K	Potassium
kg	Kilogram
KOH	Potassium Hydroxide
K ₂ SiO ₃	Potassium Silicate
LOI	Lost of Ignition
Na	Sodium
Na ₂ SiO ₃	Sodium Silicate
NaOH	Sodium Hydroxide
PS	Poly (sialate)
PSD	Particle Size Distribution
S	Solid
SEM	Scanning Electron Microscope
S/L	Solids-to-Liquid Ratio
X ₅₀	Mean Particle Size
XRD	X-ray Diffraction
XRF	X-Ray Fluorescence

Kesan Keadaan Pencampuran Terhadap Sifat Dan Ciri-Ciri Geopolimer Kaolin

ABSTRAK

Proses penggeopolimeran dengan menggunakan kaolin sebagai sumber aluminosilikat telah dijalankan. Matlamat kajian ini adalah untuk mengkaji kesan kepekatan NaOH, nisbah sumber aluminosilikat/larutan pengaktif beralkali, nisbah $\text{Na}_2\text{SiO}_3/\text{NaOH}$ dan keadaan pengawetan serta rawatan mekanikal ke atas kaolin terhadap sifat-sifat geopolimer kaolin. Keputusan kajian ini menunjukkan bahawa kepekatan NaOH 8M, nisbah sumber aluminosilikat/larutan pengaktif beralkali 1.0, nisbah $\text{Na}_2\text{SiO}_3/\text{NaOH}$ 0.32 dan keadaan pengawetan pada 60 °C untuk 72 jam adalah keadaan pencampuran optima. Rawatan mekanikal dengan menggunakan proses pengisaran telah dijalankan ke atas kaolin untuk tujuan meningkatkan kereaktifan kaolin terhadap proses penggeopolimeran. Masa pengisaran kaolin yang optimum adalah 5 jam. Rawatan mekanikal ke atas kaolin telah berjaya mengurangkan saiz zarah dan meningkatkan luas permukaan zarah serta menghasilkan geopolimer kaolin dengan kekuatan mampatan yang lebih baik (9.58 MPa) berbanding dengan geopolimer kaolin yang disintesis daripada kaolin tanpa rawatan mekanikal (5.94 MPa). Ukuran ketumpatan pukal menunjukkan bahawa geopolimer kaolin adalah bahan ringan ($< 1870 \text{ kg/m}^3$). Keboleherjaan mesti diambil kira semasa sintesis geopolimer kerana ia menjejaskan perkembangan kekuatan mampatan geopolimer kaolin. Analisis mikrostruktur (SEM) menunjukkan bahawa pelarutan kaolin dalam larutan pengaktif beralkali adalah rendah. Ini ditunjukkan oleh kehadiran zarah-zarah kaolin yang tidak bereaksi dalam mikrostruktur. Pembentukan gel geopolimer yang seragam boleh diperhatikan apabila diuji pada jangka masa panjang. Keputusan analisis komposisi unsur (EDX) menyokong bahawa geopolimer kaolin mengalami pembangunan struktur dan ini ditunjukkan dengan peningkatan nisbah Na/Al dan Si/Al. Dari analisis fasa (XRD), zeolit dapat diperhatikan dalam geopolimer kaolin selepas penggeopolimeran. Fasa amorfus geopolimer dan fasa berhablur zeolit menyumbang kepada kekuatan mampatan geopolimer kaolin. Walau bagaimanapun, intensiti fasa berhablur ini berkurangan secara beransur-ansur pada jangka masa panjang dan keputusan kajian menunjukkan bahawa kehadiran fasa berhablur ini dalam geopolimer kaolin boleh merendahkan kekuatan mampatan geopolimer. Selain itu, pengenalpastian kumpulan berfungsi (FTIR) turut menunjukkan pembentukan ikatan geopolimer yang lebih banyak dalam geopolimer kaolin apabila diuji pada jangka masa panjang. Berdasarkan keputusan kekuatan mampatan, nisbah molar oksida $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ dan $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ yang optima dalam sintesis geopolimer kaolin ialah 3.28, 0.28, 14.61 dan 0.92. Secara umumnya, kaolin mempunyai kereaktifan yang rendah dan memerlukan lebih banyak masa untuk pelarutan kaolin dalam larutan pengaktif beralkali untuk pembentukan struktur geopolimer. Tindak balas penggeopolimeran yang lambat menyumbang kepada pembangunan kekuatan mampatan yang lebih. Sebagai kesimpulan, hasil kajian ini memberi pemahaman pada sifat (kekuatan mampatan, keboleherjaan dan ketumpatan pukal) dan ciri-ciri (mikrostruktur, fasa dan kumpulan berfungsi) geopolimer kaolin. Cadangan untuk kajian masa depan adalah untuk meningkatkan kereaktifan kaolin terhadap penggeopolimeran supaya dapat meningkatkan kekuatan mekanikal.

Effect of Mixing Conditions on the Properties and Characteristic of Kaolin Geopolymers

ABSTRACT

Geopolymerization process utilizing kaolin as aluminosilicate source was performed. The goal of this study was to investigate the effect of NaOH concentration, S/L ratio, $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio, curing temperature and time as well as mechanical treatment of kaolin on kaolin geopolymers. The results showed that 8M of NaOH concentration, S/L ratio of 1.00, $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio of 0.32 and curing conditions at 60 °C for 72 hours were the optimum mixing conditions for kaolin geopolymers synthesis. In order to increase the reactivity of kaolin towards geopolymerization reaction, mechanical treatment of kaolin was conducted through milling process. The optimum milling time of kaolin was 5 hours. Mechanical treatment of kaolin has successfully decreased the particle size and increased the surface area of kaolin particles, producing mechanical-treated kaolin geopolymers with better compressive strength (9.58 MPa) compared to kaolin geopolymer synthesized with untreated kaolin (5.94 MPa). Bulk density measurement showed that kaolin geopolymers were lightweight ($< 1870 \text{ kg/m}^3$). During the geopolymers synthesis, workability must be taking into consideration since it affected significantly the strength development of kaolin geopolymers. Microstructural analysis (SEM) revealed that kaolin geopolymers only undergo low dissolution as shown by the presence of large amounts of unreacted kaolin particles in the microstructure of kaolin geopolymers. However, the formation of homogeneous geopolymer gel was observed at longer day of testing. Besides, elemental composition analysis (EDX) results supports the continuous development of geopolymer structure as indicated by the increased Na/Al and Si/Al ratios by the day of testing. Zeolites peaks appeared in kaolin geopolymers after the geopolymerization reaction as determined by phase analysis (XRD). The amorphous geopolymer and crystalline zeolite phases contributed to the strength of geopolymers. Even so, these crystalline zeolites peaks gradually decreased in intensity at longer day of testing and were found degraded the compressive strength of geopolymers. Functional group identification (FTIR) shows the formation of more geopolymer bonding in kaolin geopolymers at longer testing day. On the other hand, based on compressive strength results, the optimum oxide molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ for kaolin geopolymers synthesis were concluded at 3.28, 0.28, 14.61 and 0.92, respectively. In general, kaolin has low reactivity and it required more time for dissolution in alkaline activator solution and hence the formation of geopolymer structure. The slow rate of geopolymerization reaction led to a slow strength development of geopolymers. As a conclusion, this study provides a better understanding of the properties (compressive strength, workability and bulk density) and characteristic (microstructure, phases and functional groups) of kaolin geopolymers. Thus, for future research, it is suggested to increase the reactivity of kaolin towards geopolymerization reaction in order to improve the mechanical strength.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The history of the development of alkali-activated binders had major contribution starting from 1940's. Researcher Purdon, who activated blast furnace slag using sodium hydroxide (NaOH) concluded that alkali hydroxides act as catalysts (Pacheco-Torgal et al., 2008b). Table 1.1 summarizes the historical background of important inventions in the field of alkali-activated binders (Li et al., 2010; Roy, 1999). Referring to Table 1.1, Feret's work was considered relevant in this field; however, his work focused more on using blast furnace slag and Portland cement rather than about alkali-activated binders (Pacheco-Torgal et al., 2008b).

Table 1.1: Bibliographic history of important inventions on alkali-activated binders (Li et al., 2010; Roy, 1999).

Year	Author	Significance
1939	Feret	Slags used for cement
1940	Purdon	Alkali-slag combinations
1959	Glukhovsky	Theoretical basis of alkaline cements
1965	Glukhovsky	First called "alkaline cements"
1979	Davidovits	"Geopolymer" term
1985	Davidovits & Sawyer	Patent of "Pyrament" cement
1986	Malek et al.	Slag cement-low level radioactive wastes forms
1987	Davidovits	Ancient and modern concretes were compared

1989	Deja & Malolepsy	Resistance to chlorides was shown
1989	Roy & Langton	Ancient concretes analogs
1989	Talling & Brandstetr	Alkali-activated slag
1992	Roy & Silsbee	Alkali-activated cements: an overview
1993	Roy & Malek	Slag cement
1994	Glukhovsky	Ancient, modern and future concretes
1995	Wang & Scivener	Slag and alkali-activated microstructure
1996	Shi	Alkali-activated slag
1997	Fernandez-Jimenez & Puertas	Kinetic studies of alkali-activated slag cements
1998	Katz	Microstructure of alkali-activated fly ash
1999	Davidovits	Chemistry of geopolymeric systems, technology
1999	Palomo	Alkali-activated fly ash - a cement for the future
2000	Gong & Yang	Alkali-activated red mud–slag cement
2000	Puertas	Alkali-activated fly ash/slag cement
2001	Bakharev	Alkali-activated slag concrete
2003	Palomo & Palacios	Immobilization of hazardous wastes
2004	Grutzeck	Zeolite formation
2006	Sun	Sialite technology
2007	Duxson	Geopolymer technology: the current state of the art
2008	Hajimohammadi et al.	One-part geopolymer
2009	Provis & Deventer	Structure, processing, properties and industrial applications
2010	Daniel et al.	Effect of elevated temperatures on geopolymer
2010	Villa et al.	Alkaline activation of natural zeolite

General history of alkali-activated binders has started since 1957. Glukhovsky, a scientist working in Ukraine at Kiev Institute of Civil Engineering (KICE) in USSR