Properties of hydroxyapatite-based geopolymer synthesized from calcined kaolin

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Abstract. This research synthesized the geopolymer from calcined kaolin (600°C for 2 h in a muffle furnace) using sodium hydroxide (NaOH) and potassium hydroxide (KOH) as alkali activators. Calcium phosphate (CP) and heat treatment were introduced to study their effects on the unconfined compressive strength (USC) and crystalline phases formation of kaolin-based geopolymer. Results showed that the highest USC strength at 28 days of geopolymer was obtained from 0.4 moles of Na2O/SiO2 and K2O/SiO2 and gave strength of 12.95 and 11.56 MPa, respectively. The USC of geopolymer was observed to decrease with the addition of CP. The amounts of 5 wt.% of CP gave a 28-day strength of kaolin-based geopolymer containing NaOH and KOH activators at 9.95 and 8.88 MPa, respectively. The CP-doped geopolymers were then heated at temperatures of 500, 600, and 700°C for 2 h Results indicated that heat treatment at 600°C gave the highest USC of CP-doped geopolymer containing NaOH and KOH equal to 7.61 and 4.61 MPa, respectively with the appearance of hydroxyapatite, muscovite, and quartz in the XRD diffractograms.

1. Introduction
The fractures of bone could be caused either by minor or serious injuries. Sports injuries, traffic accidents and accidents from those that fell from a height are serious injuries that cause several fractures. Bone injuries from a fracture that cannot self-recover is usually need replacement. Bone replacement is also has an increasing demand for an increase elderly population worldwide suffered from osteoporosis. Geopolymers are inorganic materials which can be synthesized from materials containing silica and alumina. These includes calcined kaolinite clay and halloysite clay or a variety of industrial. These raw materials are activated with highly alkaline solutions such as NaOH and KOH with controlled water contents and molar compositions [1]. The Si/Al ratios of the starting materials also play a key role in geopolymerization and geopolymer properties. The optimum geopolymer properties are obtained with molar ratios SiO2/Al2O3 ~ 3.3, H2O/Na2O ~ 10 and Na2O/SiO2 ~ 0.3 [2]. The network structure of geopolymers act as support for hydroxyapatite (HAP) which is widely used as biocompatible material. It belongs to calcium phosphate (CP) compound with chemical formula of Ca10(PO4)6(OH)2. HAP is a material of varying properties depending on the preparation methods with recommended Ca/P molar ratios ranging between 1.50 and 1.67 [3].
HAP-based geopolymer has received an increase interest to be used as bone replacement material for alumina, zirconia, TZP, Mg-PSZ, TiO2 and bioglasses due to its biocompatible property [4]. This research is therefore aimed at synthesizing HAP-based geopolymer from kaolinite clay. The appropriate molar ratios of Na2O/SiO2 and K2O/SiO2 for the synthesis geopolymer, the optimum amounts of calcium phosphate and heating temperatures were investigated. The qualities of HAP-based geopolymer were determined from strength development and microstructural observations.

2. Experimental

2.1 Materials

![XRD pattern of CK.](image)

Kaolin (K) from the Mineral Resources Development Co., Ltd., Ranong province was used as starting material for the synthesis of geopolymer. The clay was calcined at 600°C for 2 h in a muffle furnace and the CK was ground using ball milling for 2 h. The ground CK was wet sieving until it was retained on sieve No. 325 less than 34% following ASTM C618-12a. The chemical compositions of CK were analyzed using X-ray Fluorescence Spectrometer (XRF) technique and is shown in Table 1. Oxides of silica (SiO2) and alumina (Al2O3) are the two main elements present in the ground CK at 53.1 and 40.8 wt.%, respectively. XRD pattern shows muscovite (KAl2(Si,Al)4O10(OH)2) and quartz (SiO2). Commercial grade chemicals in this research, including NaOH from Formosoda-p, Taiwan, KOH from UNID, Korea and CP (Ca3(PO4)2) from FDSCL, Mumbai having purity of 99, 95 and 99%, respectively were used.

| Chemical compositions (%) | SiO2 | Al2O3 | K2O | Fe2O3 | MgO | TiO2 | CaO | LOI |
|---------------------------|------|-------|-----|-------|-----|------|-----|-----|
| CK                        | 53.1 | 40.8  | 3.4 | 2.09  | 0.1 | 0.07 | 0.03| 1.25|

2.2 Sample preparation

Geopolymer samples were prepared by mixing ground CK with initial Si/Al ratio of 1.15 with Na2O/SiO2 and K2O/SiO2 at 0.15, 0.2, 0.25, 0.3, 0.35, and 0.4 molar ratios. The mixtures were mixed and transferred into cylindrical PVC molds. Geopolymer samples with NaOH or KOH activators having maximum UCS were selected for further experiment. CP were added to the selected geopolymer samples at 2.5, 5, 7.5, and 10 wt.%. The optimum amount of CP was determined from sample with highest strength and selected for further heat treatment at 500, 600, and 700°C for 2 h.

2.3 Method and testing

XRF (BRUKER AXS, S4PIONEER) were used to analyse the chemical compositions of ground CK. The unconfined compaction machine with a load cell of 5,000 N and handheld data logger (TK-32K) were used to record data following ASTM D1633-17. X-ray Diffraction diffractogram (XRD) (BRUKER AXS, D8DISCOVER) was used for microstructure observation on the formation of crystalline phases.
3. Results and discussion

3.1 Effect of the alkaline activators on the unconfined compressive strength of calcined kaolin based geopolymer

Figure 2. Effect of alkaline activators on UCS of CK based geopolymer (a) NaOH (b) KOH.

Variation of NaOH solution at Na$_2$O/SiO$_2$ molar ratio on UCS development of CK-based geopolymer is shown in Figure 2(a). At 7 days of curing, UCS at Na$_2$O/SiO$_2$ molar ratio of 0.15, 0.2, 0.25, 0.3, 0.35, and 0.4 was 0.93, 1.91, 3.20, 4.77, 5.74 and 6.95 MPa, respectively and increased to 1.54, 2.66, 4.58, 7.43, 9.28 and 12.95 MPa after curing for 28 days. Figure 2(b) shows the strength development of CK-based geopolymer with KOH at K$_2$O/SiO$_2$ molar ratio. Strength of CK-based geopolymer after curing for 7 days was 0.49, 0.92, 1.50, 2.45, 3.69 and 5.08 MPa. and increased to 0.66, 1.23, 2.30, 4.62, 8.42 and 11.56 MPa at the age of 28 days for samples containing K$_2$O/SiO$_2$ at molar ratio of 0.15, 0.2, 0.25, 0.3, 0.35 and 0.4 mol, respectively. The maximum strength was obtained from CK-based geopolymer with Na$_2$O/SiO$_2$ and K$_2$O/SiO$_2$ molar ratio of 0.4 and gave strength of 12.95 and 11.56 MPa after curing for 28 days. Results showed that strength increased with the increase of Na$_2$O/SiO$_2$ or K$_2$O/SiO$_2$ molar ratio and curing time. The strength of all samples containing KOH were lower than NaOH.

Strength development of CK-based geopolymer is resulting from the high alkalinity of NaOH and KOH activators leading to the dissolution of SiO$_2$ and Al$_2$O$_3$ from CK. The soluble silicates and aluminates react with Na$^+$ and K$^+$ cations from the alkali activator and produced sodium or potassium aluminosilicate gel [5] which contributes to strength. In addition, a smaller ionic radius of Na$^+$ cation compares to K$^+$ cation play an essential role in an increase solubility from CK. As a result, an increase degree of geopolymerization was obtained, and thus higher strength of CK-based geopolymer activated with NaOH was observed. From the experimental results, CK-based geopolymers with Na$_2$O/SiO$_2$ and K$_2$O/SiO$_2$ molar ratio of 0.4 were selected for further study.

3.2 Effect of calcium phosphate on the compressive strength of hydroxyapatite based geopolymer

Strength development of CK-based geopolymer activated by NaOH as a function of various amounts of CP is shown in Figure 3(a). The addition of CP at all levels resulted in a reduction of strength development of CK-based geopolymer at all curing duration. A similar observation was reported by previous research and found that the inclusion of CP increased porosity during geopolymerization process leading to a decrease of strength [6,7]. The highest strength was obtained at 5 wt.% of Ca$_3$(PO$_4$)$_2$ addition and gave strength 9.95 MPa at 28 days. Similar variations in strength development were obtained from CK-based geopolymer activated by KOH when Ca$_3$(PO$_4$)$_2$ was added at 0, 2.5, 5.0, 7.5
and 10.0 wt.% shown in Figure 3(b). Results showed that strength development of geopolymer activated by KOH was lower than NaOH at all levels of Ca$_3$(PO$_4$)$_2$ addition and at all curing durations. Tchakouté et al. [8] reported that CK-based geopolymer mixed with 0, 2, 4, 6, 8 and 10 wt.% of CaHPO$_4$ gave the highest USC 48.4 MPa at 6 wt.% addition of CaHPO$_4$. The reduction of the USC related to the excess PO$_4$ units in the system. This phenomenon results in an imbalanced charge of (PO$_4$)$_3^-$ ions leading to a weakening of the microstructure and thus reduce strength of the geopolymers. Therefore, the addition of 5 wt.% of Ca$_3$(PO$_4$)$_2$ to CK-based geopolymer activated with NaOH and KOH was selected for the heat treatment study.

![Figure 3. UCS of CK-based geopolymer with Ca$_3$(PO$_4$)$_2$ (a) NaOH activator (b) KOH activator.](image)

3.3 Effect of heat treatment on strength of CK-based geopolymer

![Figure 4. UCS of CK-based geopolymers after heat treatment under various temperatures.](image)

CK-based geopolymer activated added 5 wt.% of Ca$_3$(PO$_4$)$_2$ with NaOH and KOH gave the strength of 7.51, 7.61, 4.92 and 3.78, 4.61, 3.77 MPa when subjected to heat treatment at 500, 600 and 700°C, respectively. (Figure 4) The highest strength was found at 600°C for CK-based geopolymers activated with both NaOH and KOH. Thokchom et al. [9] investigates the effects of heat treatment between 300 to 700°C on the pore structures of geopolymer paste. In addition, Kenneth et al. [2] reported that heat treatment reduced cracking of geopolymer and pH value of simulated body fluid (SBF) after soaking.

3.3 XRD results of CK-based geopolymer

The XRD patterns of CK-based geopolymer with both NaOH and KOH and addition of 5 wt.% of Ca$_3$(PO$_4$)$_2$ (CKN and CKK) were shown in Figures 5. Peaks of sodium aluminum silicate (SA), HAP, muscovite and quartz appeared in CKN. The formation of SA resulted in development of UCS of CK-based geopolymer. The appearance of HAP, potassium aluminum silicate (PA), calcium phosphate hydrate, muscovite, and quartz were observed from CKK. The SA and PA developed UCS of CKN and CKK. XRD pattern of CK-based geopolymer with both NaOH and KOH and added 5 wt.% of Ca$_3$(PO$_4$)$_2$ after heat treatment at temperature of 600°C (CKN600 and CKK600). Heat treatment reduced the
intensity of the peaks for SA, HAP, muscovite, and quartz with the appearance of calcium aluminum silicate hydrate (CASH) in CKN600. While XRD pattern of CK600 found HAP, calcium aluminum silicate, muscovite and quartz. Other research found HAP after soaking in SBF solution [2, 10].

Figure 5. XRD pattern of CK-based geopolymer with 5 wt.% Ca₃(PO₄)₂ addition (a) NaOH activator (b) NaOH activator after heat treatment at 600°C (c) KOH activator (d) KOH activator after heat treatment at 600 °C

4. Conclusions
This research found that the highest strength of CK-based geopolymer was obtained from a sample with Na₂O/SiO₂ and K₂O/SiO₂ molar ratio of 0.4, at 5 wt.% addition of CP and heat treatment at the temperature of 600°C. Heat treatment at the temperature of 600°C resulted in the formation of crystalline hydroxyapatite within the geopolymer network synthesized from ground CK which play an important role as support for hydroxyapatite. Further research is on-going to study the suitability of using hydroxyapatite-based geopolymer as bio-ceramic materials to replace bone.

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