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The effects of synthesized calcium phosphate compounds on the mechanical and microstructural properties of metakaolin-based geopolymer cements

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HIGHLIGHTS

- Brushite and hydroxyapatite were prepared from oyster shell powder and phosphoric acid solution.
- Brushite and hydroxyapatite were used as additive for the replacement level of metakaolin.
- The resulting powders were used for producing geopolymer cements.
- The strengths of geopolymer cements containing brushite were in the range 40–48 MPa.
- The strengths of geopolymer containing hydroxyapatite were in the range 28–43 MPa.

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ABSTRACT

Dicalcium phosphate dihydrate (DCPD) and hydroxyapatite (HAP) were prepared from oyster shell powder and phosphoric acid solution as raw materials using sol-gel process in order to study the influence of calcium phosphate compounds on the mechanical and microstructural properties of metakaolin-based geopolymer cements. The synthesized DCPD and HAP with molar ratio Ca/P equal to 1.00 and 1.65, respectively, were used as additives for replacement of metakaolin (0, 2, 4, 6, 8 and 10 wt%) and the resulting powders were used for producing geopolymer cements. The compressive strengths of geopolymer cements containing DCPD were in the range 40–48 MPa with increasing DCPD content, but when 10 wt% was used, the strength fell to 26 MPa. Similar results were obtained for HAP addition with a decrease of the compressive strength at 8 wt%. The ESEM images of geopolymers containing 4–10 wt% of HAP showed some non-reacted or partially reacted particles that do not well connect to the matrix. Samples of geopolymer with 4–8 wt% of DCPD present a lower number of unreacted particles and the matrix appeared denser than that of the control geopolymer cements. The use of calcium phosphate compounds such as brushite and hydroxyapatite led to the overall improvement in compressive strength and contribute to the densification of the structure of geopolymer cements. On the other hand, the addition of 4% of HAP and 10% of DCPD resulted in a large amount of hydroxyapatite and brushite, respectively in the systems. The matrix appear less dense indicating that a fraction of calcium phosphate addition at the aforementioned level was excessive.

1. Introduction

Geopolymer cement is a binder system that hardens at room temperature like regular mortars, concretes and pastes from Portland cement commonly obtained by mixing raw aluminosilicate

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material (such as clay mineral, metakaolin, fly ash, volcanic ash, slag, etc.) with a hardener [1] The hardener may be a sodium silicate solution or, more rarely, phosphoric acid solution. The geopolymer network is then based on poly(sialate) when sodium or potassium silicate is used as hardener or poly(phosphosiloxane) when phosphoric acid is used as a hardener [2]. Both systems have been studied separately, their mechanical and microstructural characteristics reported along with reaction mechanism. It has been reported that geopolymer obtained from phosphoric acid solution developed better compressive strength than those in sodium silicate solution [3]. The reaction mechanism that occurs when sodium silicate is used as hardener includes the alkalization, depolymerization of aluminosilicates in silicate and aluminate species followed by polycondensation of these species, reticulation or networking and finally geopolymer solidification. In the phosphoric acid solution, the species that condense are silicate (SiO_4^{4-}) and phosphate (PO_4^{3-}) [3].

Different calcium sources (slag, limestone, oyster shell, wollastonite, etc.) have been used to investigate its effects on geopolymer composition and mechanical properties [4–8]. It has been reported that depending on the reactivity of the calcium sources and alkalinity of hardener used, the geopolymer cement could be a mixture of polysialate or sodium, calcium aluminosilicate hydrate (N, C-A-S-H) and calcium silicate hydrate (C-S-H). This system included the substitution of sodium by calcium during the condensation reaction and combined with the formation of a distinct calcium phase. The coexistence of these phases in the geopolymer matrix has been proved to be beneficial for strength development. Some researchers such as Derrien et al. [9] and MacKenzie et al. [10] commonly used commercial calcium phosphate compounds such as tricalcium phosphate ($Ca_3(PO_4)_2$) and hydroxyapatite for producing an inorganic polymer that can be used as bioactive materials for osseous bone applications. Such system is interesting as calcium could substitute sodium or potassium in the network, and phosphate (PO_4^{3-}) replace some silicates (SiO_4^{4-}) during the formation of the geopolymer network leading to a hybrid system based on Ca, Na-poly(sialate) and poly(phospho-siloxane) networks. However, no literature discuss the influences of other calcium phosphate components such as brushite, monetite, and hydroxyapatite on the mechanical and microstructural properties of metakaolin-based inorganic polymer cements.

This work aims to investigate the effects of calcium phosphate compounds (brushite, and hydroxyapatite) on the mechanical and microstructural properties of metakaolin-based geopolymer cements. The calcium phosphate compounds were obtained from oyster shell, phosphoric acid solution, and water. No previous study has characterized the synthesis of geopolymer cements using calcium phosphate compound as an additive for construction and building materials. The synthesized calcium phosphate such as brushite and hydroxyapatite with molar ratio Ca/P equal to 1.00 and 1.65, respectively were used as additives for replacement level of metakaolin (0, 2, 4, 6, 8 and 10%). These calcium phosphates were prepared using oyster shell powder as low-value calcium-rich waste materials.

2. Materials and experimental methods

2.1. Materials

The kaolin used in this work was extracted from Bomkoul (Douala sub-basin, Cameroon) and the oyster shell was picked up in the coastal area of Cameroon. Bomkoul and the seaside are located in the Littoral region of Cameroon. Kaolin and oyster shell were previously studied by Elimbi et al. [11] and Djobo et al. [8,12], respectively. They reported that kaolin is mainly composed of kaolinite associated to quartz, illite, hematite, and anatase as impurities and oyster shell is mainly constituted of calcium carbonate/calcite. The chemical compositions of kaolin and oyster shell are given in Table 1. Before using the oyster shell, the organic matter has been removed and the shells were dried in air. The dried shells were calcined at 500 °C in a programmable electric furnace (Nabertherm, Mod_LH60/14) for 2 h with a heating and cooling rate of 5 °C/min. The calcined oyster shell and kaolin were crushed separately in a ball mill with a porcelain jar and microspheres of high-grade alumina as grinding medium, then passing through a 90 μm, obtaining oyster shell powder (OSA) and the powder of kaolin (BO1), respectively. The powder of kaolin was calcined at 700 °C using the aforementioned furnace for 4 h with a heating and cooling rate of 5 °C/min to obtain metakaolin (MK). Commercial phosphoric acid (H_3PO_4 85%, puriss. p.a., Reag. ACS, Reag. ISO, Reag. Ph. Eur. d = 1.60) was used as a chemical reagent. Commercial silica fume, SiO_2,-xH_2O (Merck, N^0 10 279-57-9) was used to prepare the hardener or reactive ingredient.

2.2. Experimental methods

2.2.1. Preparation of calcium phosphate components: Brushite and hydroxyapatite

Brushite and hydroxyapatite were prepared by adding firstly oyster shell powder into distilled water in order to obtain calcium hydroxide ($Ca(OH)_2$), as can be seen in the following reaction:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (1)$$

The obtained $Ca(OH)_2$ was mixed with a phosphoric acid solution using the molar ratio Ca/P equal to 1.00 and 1.65 to get brushite and hydroxyapatite pastes, respectively using the following reactions:

$$Ca(OH)_2 + H_3PO_4 \rightarrow CaHPO_4.2H_2O \text{ Brushite gel} \quad (2)$$

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 12H_2O \text{ Hydroxyapatite gel} \quad (3)$$

The aforementioned pastes were dried for 4 h in an oven at 80 °C and the obtained powders of brushite and hydroxyapatite were denoted DCPD and HAP, respectively. It is important to note that oyster shell is calcined at 500 °C, hence its probably contained the remnant of carbonates.

Table 1
Chemical composition of BO1 and OSA in mass percent (wt%).

Oxide	BO1	OSA
SiO_2	41.46	0.30
Al_2O_3	31.47	0.19
Fe_2O_3	7.65	0.19
K_2O	0.51	–
TiO_2	1.50	–
MgO	0.65	–
Na_2O	0.69	0.57
CaO	0.15	74.73
SO_3	–	0.11
P_2O_5	0.09	–
ZnO	–	0.01
MnO	0.06	–
Rb_2O	–	–
SrO	–	0.32
ZrO_2	–	–
As_2O_3	–	0.27
Cl^-	–	0.12
LOI	15.76	23.23

LOI: Loss on ignition at 1000 °C.