

Bioactivity enhancement of calcined kaolin geopolymer with CaCl_2 treatment

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ABSTRACT: This paper reports that surface treatment with CaCl_2 enhances the bioactivity of a calcined kaolin geopolymer. Calcined kaolin, NaOH solution, sodium silicate solution, and heat curing were used to form geopolymer pastes. A soaked-treatment method was applied to the geopolymer samples using CaCl_2 solution as the ion exchange agent. The bioactivity of the material was determined by the simulated body fluid (SBF) in vitro testing method. Scanning electron microscope images showed a dense apatite formation on the treated geopolymer surface after SBF immersion for only 3 days. The CaCl_2 treatment promoted compressive strength and enhanced bioactivity by accelerating apatite precipitation and slowing down the rise in pH.

KEYWORDS: aluminosilicate, metakaolin, apatite, SBF

INTRODUCTION

A geopolymer is an aluminosilicate amorphous structure that results from the polycondensation of inorganic compounds¹. A geopolymer is defined as an alkali-activated material and is produced through the reaction of aluminosilicate materials with an alkaline activator, which is usually a concentrated alkali hydroxide, silicate, carbonate, or sulphate². Fly ash, ground granulated blast furnace slag, and calcined kaolin are good source materials. Geopolymers can be produced and used as a cementitious material similar to Portland cement as they are strong and durable. Research on the use of geopolymers has been extended to many fields such as fire resistant construction materials³, and smart materials⁴.

Cementitious materials have various applications such as sensing and electrical components⁵, self-cleaning material with photo catalysis properties⁶, and biocompatible materials^{7–9}. Cement and ceramic have been studied in application of biocompatible material and generally used as “in vitro” test method, the outside body test using simulated body

fluid (SBF)^{10,11}. The use of mechanically compliant interface with living tissue was first observed in 1969 and is now referred as ‘bioactivity’¹². Bioactivity of implant materials is usually identified by precipitation of biolayer on material surface called apatite layers¹³. These biocompounds are connectable bonding between material and living bone and play significant role in nucleation sites for new bone growth¹⁴. Apatite layers are commonly composed of calcium and phosphate such as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ hydroxyapatite (HA), $\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3)(\text{H}_2\text{O})$ carbonate apatite, and $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ chlorapatite¹⁵. Furthermore, the change in pH condition of SBF solution after soaking the material has an important effect on the biocompatibility. High pH changes at the surface of the implant material can harm living cells¹⁶.

Recently, biocompatible metakaolin-aluminosilicate materials have been tested both in vivo^{17–19} and in vitro^{20–23}. For implant applications²⁴, geopolymers have been shown to be bioactive with low ion leakage, although the possible leaching of aluminium can result in toxicity²¹. Kaolinite, a good source material for making geopolymers, has been

extensively used as a pharmaceutical excipient. The study of geopolymers for implant material indicates the problem of low bioactivity. The incorporation of $\text{Ca}(\text{OH})_2$ in geopolymers can promote the apatite forming ability²¹. The presence of CaCO_3 enhances the apatite forming ability by inducing the precipitation of phosphate ions¹⁰. CaCl_2 and white Portland cement produce nontoxic treated cement paste⁸, and increase the bioactivity by showing high hydroxyapatite formation after immersion in SBF solution²⁵. For geopolymer material, adding of CaCl_2 can be applied in a small amount around 1% of binder because of the rapid hardening²⁶ and is not sufficient to gain high bioactivity. Since geopolymer structure has a weak sodium bond and this can be leached out almost completely²⁷, thus it can be charge-balanced with other cations by treating with chloride solution of the desired cations²⁸. Direct contact of CaCl_2 solution provides Ca^{2+} cations to the surface of geopolymer and promotes the precipitation of reactive calcium compound for bioactivity and simultaneously enhances strength and durability of geopolymers²⁹.

This paper presents the use of CaCl_2 to enhance the apatite forming ability of calcined kaolinite geopolymer. The knowledge would be instrumental for future development of calcined kaolinite geopolymer for biomaterial applications.

MATERIALS AND METHODS

Materials

Kaolin from Ra Norng province in southern Thailand was calcined at 600 °C for 6 h to generate high reactivity calcined kaolin (CK)³⁰ and used as a source material. The CK consisted of 60% SiO_2 , 34% Al_2O_3 , 0.1% CaO , 0.9% Fe_2O_3 , 0.2% MgO , 0.2% Na_2O , 0.1% SO_3 , and 1% LOI. NaOH with concentration of 10 molar and sodium silicate with 15% Na_2O , 33% SiO_2 , and 52% H_2O were used as alkali activators. CaCl_2 solution (CC) with 0.5 molar concentration prepared from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and deionized water was used for treatment³¹. For the biocompatibility test, a simulated body fluid solution (SBF) with ion concentration similar to human blood plasma¹³ was prepared and used.

Sample preparation

Prepared CK was mixed with NaOH for 5 min and then mixed with sodium silicate for another 5 min. The sodium silicate: NaOH ratio of 1 and liquid to binder ratio of 1 were used. Geopolymer paste was cast into 25 × 25 × 25 mm acrylic moulds for

compressive strength test and 10 mm diameter and 2 mm thick disks for bioactivity test. The fresh geopolymer pastes were compacted for 10 s with the aid of a vibrating table. The moulds were left in a controlled 23 °C room for 1 h, and then wrapped with plastic film and cured at 60 °C for 24 h. The specimens were left to cool down and demoulded. For the control samples, they were also wrapped with plastic film and kept in the controlled 23 °C room. For CaCl_2 treatment, the samples were treated by soaking in CC solution for 24 h at 23 °C³². The samples were then dried in a desiccator for 12 h and wrapped with plastic film and stored in the controlled 23 °C room.

In vitro test

At the age of 7 days, the treated and untreated discs were soaked in SBF solution with solution volume to sample surface of 0.1³³. The immersed duration was left for 28 days with temperature controlled at 37 °C similar to human body¹³. The pH values of SBF solutions were monitored during the soaking.

Other tests

Geopolymers were tested for compressive strength at 7 days in accordance with ASTM C109³⁴. The reported results are the average of three samples. Bioactivity characterization of geopolymer surface was made using JEOL JEM-5910LV scanning electron microscopy (SEM). Identification of pH change after sample immersed in SBF was done by ion electrode pH meter. The X-Ray Diffraction (XRD) experiments were performed with step of 0.0229° and step time of 240.5 s at 25 °C using Bruker's TOPAS software to confirm the chemical compound of geopolymer. Fourier transform infrared (FTIR) spectroscopy was also performed on the geopolymer samples.

RESULTS AND DISCUSSION

Compressive strength and surface structure

The 7 days compressive strength of control and treated pastes were 49.9 and 53.7 MPa, respectively. These strength values are comparable to the other reported compressive strengths of calcined kaolinite geopolymers^{35,36}. The treatment by CaCl_2 had a positive effect on the strength development. The increase of strength was due partly to the additional wet curing of the samples soaked in the CaCl_2 solution. The immersion caused sustained water on the surface of geopolymer and affected the geopolymerization³⁷. Moisture curing of geopolymer results

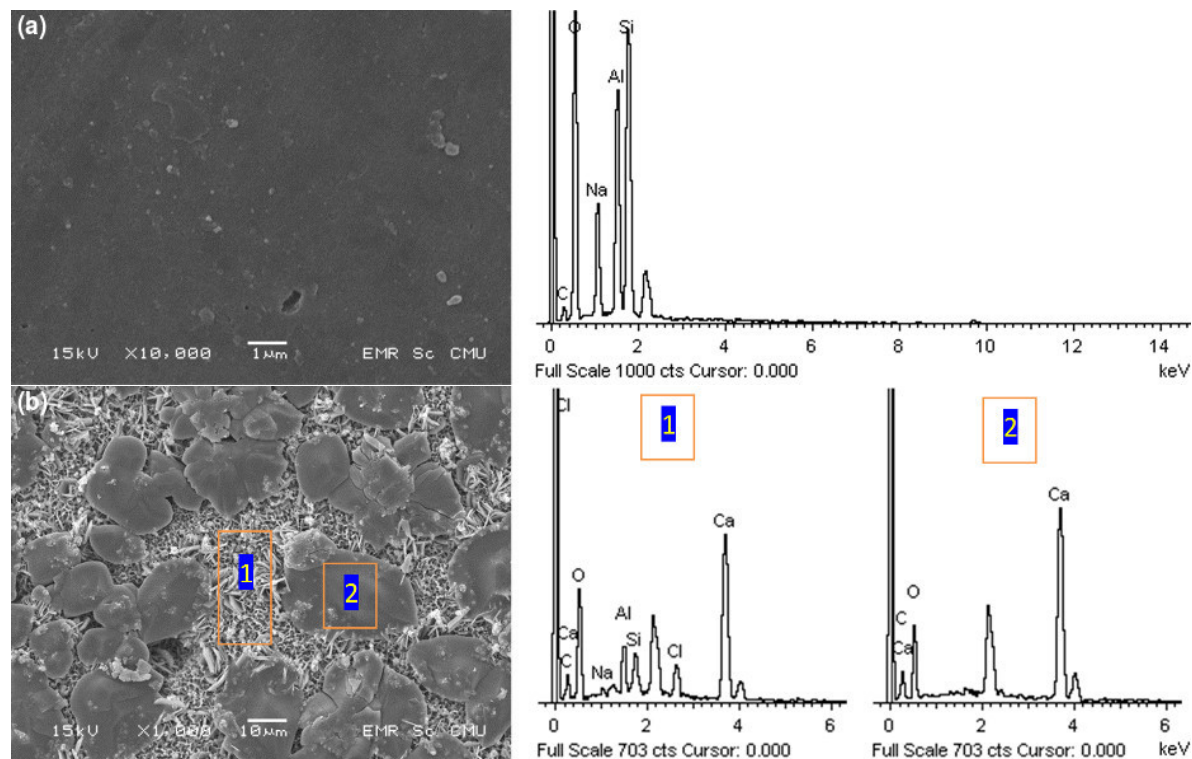
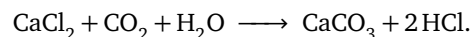


Fig. 1 SEM images of geopolymer surfaces before soaked in SBF solution; (a) control sample, (b) treated sample.

in a slight increase in strength compare to ambient curing condition³⁸. Immersion of geopolymer in CaCl_2 solution increased the amount of calcium ion absorption and the chemically bonds with geopolymer components similar to the behaviour of cement material^{31,32}. The surface hardness of the geopolymer was improved due to the ions charge-balancing between Ca^{2+} and Na^+ cations. The calcium component consequently precipitated and improved surface hardness. This thus favourably affected the strength development of geopolymer paste.

The results of the SEM studies on the geopolymer surfaces are shown in Fig. 1. The surface of control paste was relatively smooth with EDS spectra of Si, Al, O, and Na elements (Fig. 1a). These elements are the composition of kaolinite geopolymer^{36,39}. After CaCl_2 treatment, the surface structures showed the clear deposits of calcium compounds as shown in Fig. 1b with two different crystallized forms. The first form was the tiny crystals in area 1 which were the plates of calcium and chloride compounds precipitated in the geopolymer structure. Related EDS spectra showed mainly high peaks of Ca and Cl and low content of Na, Si, Al, and C elements. The second form was the large crystal

plate in area 2 which was identified as CaCO_3 by the EDS spectra of Ca, C, and O elements and by high peak of calcite in XRD patterns in Fig. 2. The results thus show that CaCl_2 was absorbed on kaolinite geopolymer surface by solution soaking. The follow-on induced carbonation reaction with CO_2 from the atmosphere resulted in the formation of CaCO_3 at the paste surface²⁶:



The weak sodium can be leached out from the geopolymer structure²⁷ and charged-balance with calcium cations from CaCl_2 ²⁸. This phenomenon promotes Ca^{2+} to form at the surface of geopolymer in the form of reactive calcium compounds and enhances the strength development²⁹. The use of CaCl_2 promotes the strength of geopolymer and the biocompatible layers on geopolymer surface and thus results in a strong interfacial zone between geopolymer and new growth apatite.

Apatite formation after SBF immersion

The surface characteristic of geopolymer after soaking in SBF solution is presented in Fig. 3. For the control mix, the apatite-like layer formed after

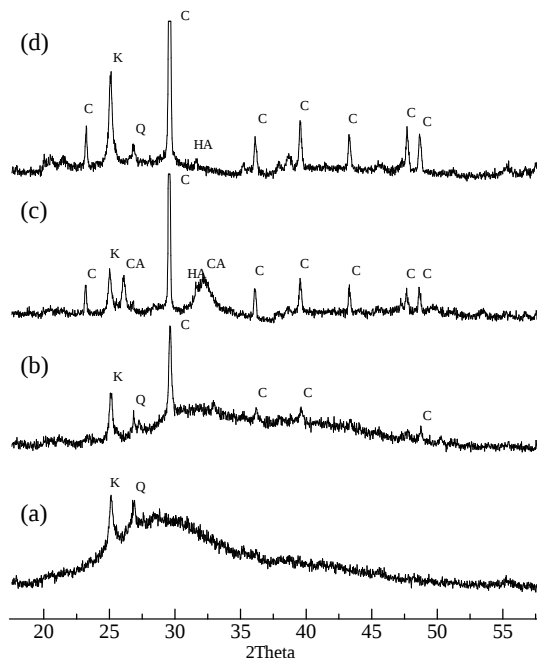


Fig. 2 XRD patterns of geopolymer paste discs; (a) control; (b) treated sample; (c) treated sample after 3 days in SBF; (d) treated sample after 28 days in SBF

28 days of immersion was still not clearly visible (Fig. 3a), but the EDS spectra presented Ca and P as possibly precipitated from SBF solution. Geopolymer without CaCl_2 treatment was poor in bioactivity due to the lack of Ca^{2+} ions to act as nucleation sites for apatite precipitation. For the CaCl_2 treated geopolymer after 3 and 28 days of soaking in SBF, spherical particles of approximately $10\ \mu\text{m}$ in diameter of apatite phase were clearly observed covering the entire paste surface (Figs. 3b and 3c). The Ca/P molar ratio from EDS analysis was 1.51 and 1.56 represented precipitated HA and/or β -tricalcium phosphate (β -TCP)^{40,41}. The morphology of the formed bioapatite layer was similar to the other published results^{42,43}. The crystallographic study by XRD technique presented in Fig. 2 indicated the high amount of observed hydroxyapatite and chlorapatite on the CaCl_2 treated sample after soaked in SBF. The pattern of observed hydroxyapatite crystal in X-ray patterns was similar to the previous published results⁴⁴. The X-ray pattern also displayed high CaCO_3 peak at $29.5^\circ\ 2\theta$ which correlated well with the FTIR result. The presence of high CaCO_3 at the geopolymer surface is very positive in promoting the high apatite precipitation¹¹. This showed that calcium compound especially CaCO_3 deposited on the geopolymer surface as a result of

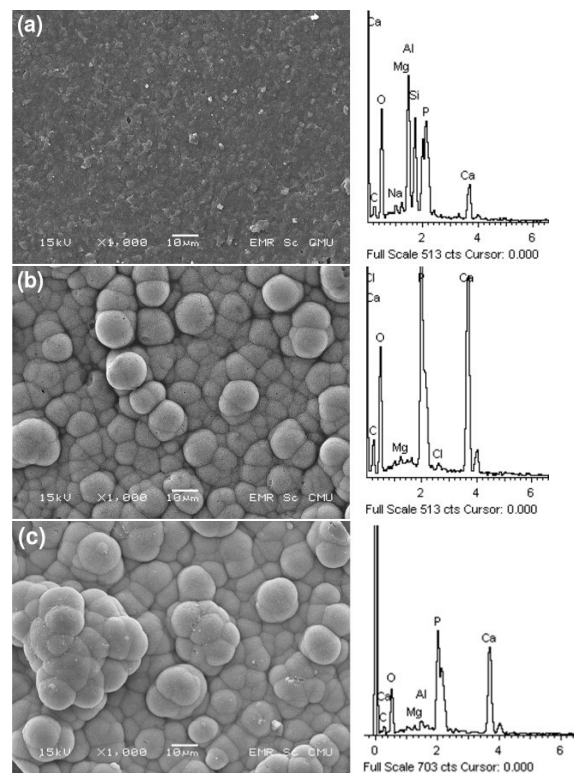


Fig. 3 SEM images of geopolymer surfaces after soaked in SBF solution; (a) control sample after 28 days in SBF solution; (b) treated sample after 3 days in SBF solution; (c) treated sample after 28 days in SBF solution.

CaCl_2 treatment¹⁰. Metakaolin geopolymer without calcium treatment exhibited only a small apatite forming after immersion for 21 days⁴⁵. The treatment by CaCl_2 improved the forming of apatite as dense apatite was formed after only 3 days of soaking in SBF compared to the 7 days of soaking for calcium rich white cement⁴⁶. The fast forming of hydroxyapatite is considered advantageous for implant materials^{47,48}.

The EDS spectra as shown in Fig. 3 suggested the forming of dendrite of carbonate substituted hydroxyapatite⁴⁹ which was rich in Ca, P, C, Cl, and Mg similar to glass ceramic systems⁵⁰. Side view of apatite growing by SEM image as shown in Fig. 4 showed the interfacial zone of geopolymer and formed apatite. Microstructure of geopolymer matrix on the left showed a dense surface with platy shape of kaolinite as also reported elsewhere⁵¹. The apatite structure on the right was very dense and covered the thickness around $15\ \mu\text{m}$. The side view clearly identified the good apatite forming and

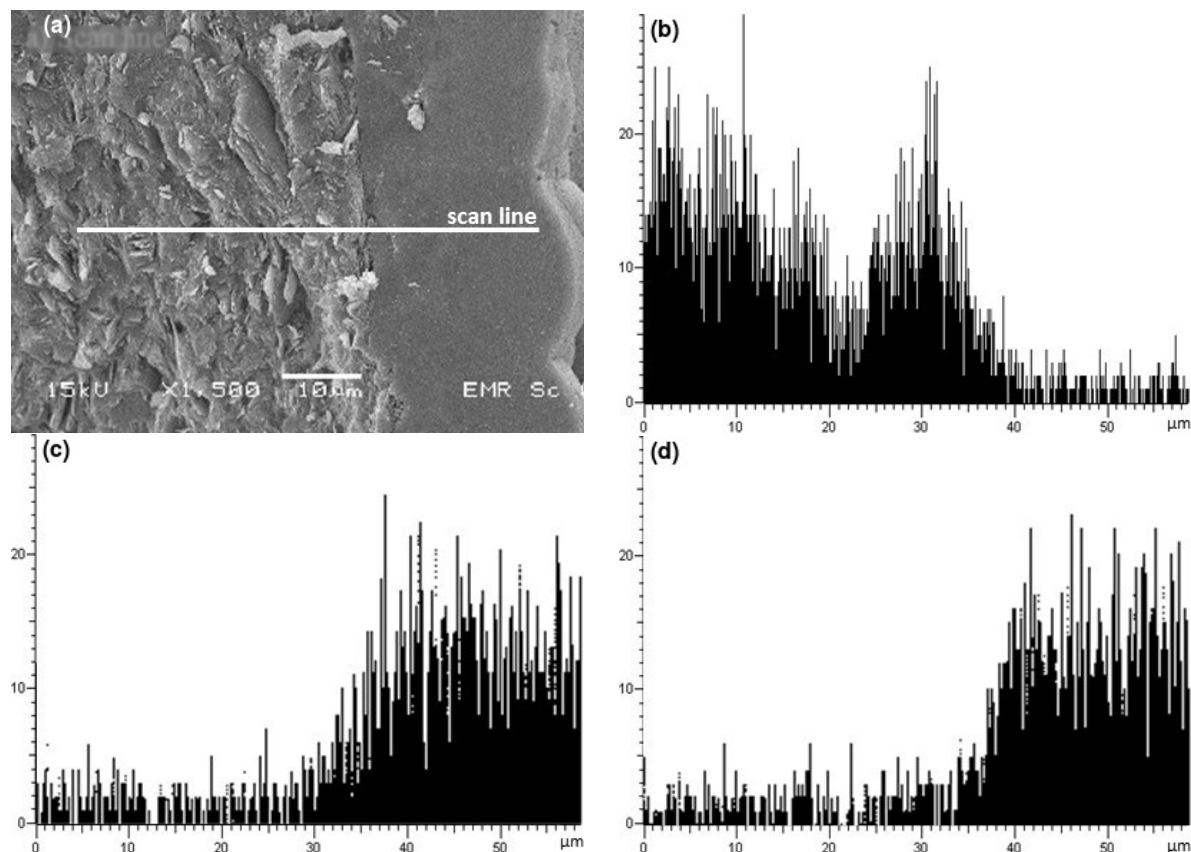


Fig. 4 (a) Side view of apatite forming by SEM and line analysis of (b) Si, (c) Ca, and (d) P.

interface bonding. Additionally, the line analysis showed distributions of important elements, viz., Ca, P, and Si across the transition zone. For Ca and P, spectrum line peak raised at transition zone of geopolymer and apatite layer was clearly evident and the results correlated well with the SEM image. For Si, the spectrum showed migration of Si by illustrating the spectrum dropped towards the transition zone and increased again at the transition zone. When material came into contact with SBF solution, the Si-OH rich layer was formed and supported the migration of Ca^{2+} ions to be incorporated with PO_4^{3-} ions from SBF solution and formed calcium rich film which continuously precipitated as apatite layer^{52,53}. It had also been shown that the high reactivity of apatite forming produced a thick silica gel layer between the apatite layer and the glass material⁵⁴. The FTIR spectra of geopolymer after 28 days soaking in SBF solution is shown in Fig. 5. CaCl_2 treated sample presented PO_4^{3-} band peak at 1030 cm^{-1} and apatitic PO_4^{3-} at 620 and 578 cm^{-1} . The phosphate absorption bands of PO (cryst) of PO_4^{3-} indicated the formation of apatite^{55,56}. The

presence of high PO band peak confirmed the enhancement of apatite precipitation on geopolymer surface with CaCl_2 treatment. The SBF soaking of 28 days significantly showed higher band peak size of PO at the wavenumber around 1030 cm^{-1} than 3 days of soaking which represented the additional precipitation of apatite layer on sample surface with time. Moreover, treated sample showed the bending vibration peak of CO at 870 cm^{-1} corresponding to CO_3^{2-} functional group of CaCO_3 . The presence of CaCO_3 was an indication of the promotion of apatite forming. For untreated samples, no apatitic or CaCO_3 band peaks were significantly observed. Similarly, the SEM results showed no crystalline shape in the untreated sample.

The pH of the SBF solution after soaking for up to 28 days is shown in Fig. 6. Measured pH value of SBF solution increased from 7.40–7.81 for untreated paste. For the paste with CaCl_2 treatment, the increase in pH value was smaller at 7.59. This finding was in line with the other published results which reported the lower pH values of SBF solution for the CaCl_2 treated samples than those of other

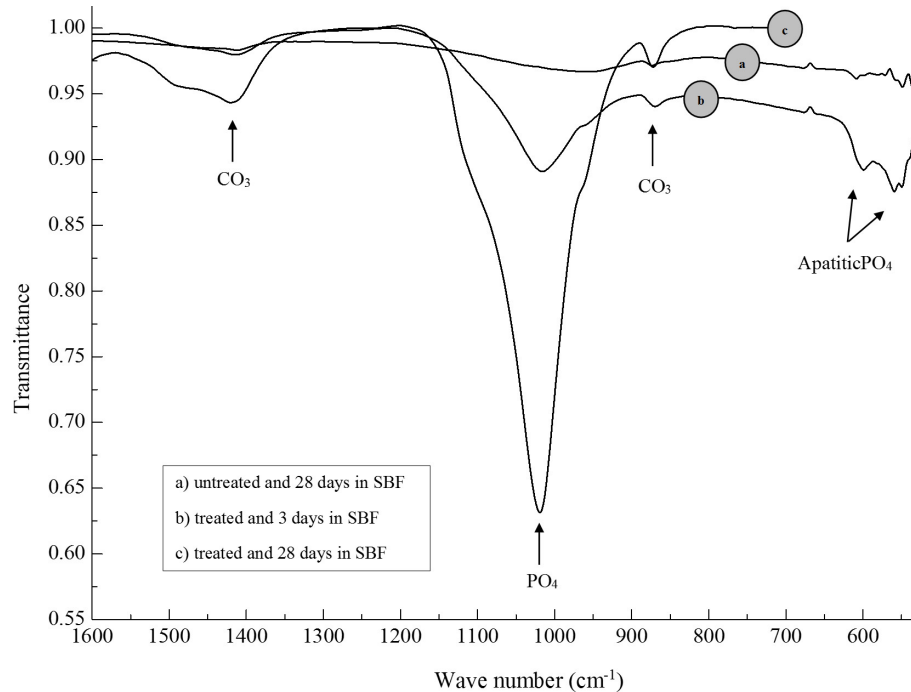


Fig. 5 FTIR spectra of geopolymer surface.

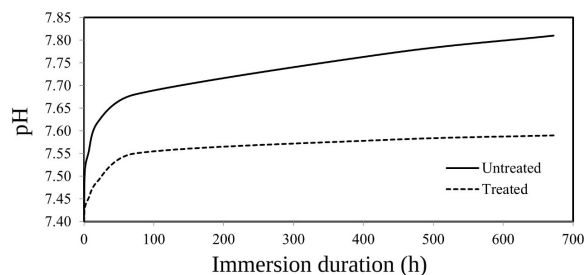


Fig. 6 pH of SBF solution immersed with geopolymer discs.

cementitious materials^{10,57}. The pH increase was a typical result of leaching of NaOH from material to SBF solution. The treatment process possibly reduced leaching ability of NaOH due to the forming of calcium compound layer. It can be concluded that CaCl₂ treatment of geopolymer samples lowers the pH of the immersed solution and additionally promote the geopolymer surface for the growth of apatite.

CONCLUSIONS

Treatment of calcined kaolin geopolymer surface by soaking in 0.5 molar concentration of CaCl₂ · 2H₂O solution for 24 h can embed calcium, chloride, and carbonate compounds to the material surface.

These reactive calcium rich layers promote the apatite precipitation. A good apatite forming on treated calcined kaolin geopolymer surface was obtained after 3 days in SBF immersion. The CaCl₂ treatment not only enhances the early compressive strength by the process of moist curing but also renders low pH induction after the contact with SBF solution. This high rate of apatite forming and low alkalinity are preferable for the implant material.

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