

# Sulfuric Acid Resistance of Geopolymer Mortars from Co-combustion Residuals of Bamboo and Kaolin

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This study presents an investigation of the durability and microstructure of geopolymer mortars from co-combustion residuals of bamboo and kaolin when exposed to 5% sulfuric acid solution for 2, 4, and 6 weeks, respectively. Geopolymer mortars sized 5 x 5 x 5 cm were prepared from co-combustion residuals of bamboo and kaolin with alkaline activators, i.e. mixture of 10 N potassium hydroxide solution and sodium silicate solution, and cured at 60 °C in oven for 8 hours and then at room temperature for 28 days. Mortars from ordinary Portland cement were also prepared as control mortars. The parameters studied were visual appearance changes, mass changes, compressive strength changes, and microstructure changes. Microstructure changes were examined using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The results revealed that geopolymer mortars showed better sulfuric acid resistance compared to ordinary Portland cement mortars in terms of lower mass loss and lower compressive strength loss.

**Keywords:** bamboo, co-combustion residuals, geopolymer, kaolin, mortar, sulfuric acid resistance

## INTRODUCTION

Geopolymer, inorganic polymer with Si-O-Al bonds, has gained considerable attention as Portland cement substitute lately. Geopolymer has advantages over Portland cement, i.e. geopolymer production can use solid waste containing alumino-silicate oxides such as fly ash and slag as raw materials and takes place at low

temperature (below 100 °C) (Duxson et al. 2007). Moreover, geopolymer production can reduce by 80% CO<sub>2</sub> emissions compared to Portland cement production (van Deventer et al. 2012). Geopolymer has also shown to have high compressive strength as well as high fire and acid resistance (van Deventer et al. 2012).

Resistance to acid environment is one of the characteristics that should be

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possessed by building materials. Acid environment can be caused by acid rain, acid groundwater, acid solution from chemical and mining industries, etc. Studies of acid resistance have been done on geopolymer prepared from fly ash (Bakharev 2005, Allahverdi and Skvara 2005), bottom ash (Sata et al. 2012), slag (Bernal et al. 2012), palm oil fuel ash (Ariffin et al. 2013), rice husk ash (Kim et al. 2014), and metakaolin or calcined kaolin (Bouguermouh et al. 2017).

In this study, geopolymer mortars were prepared from co-combustion residuals of bamboo and kaolin with alkaline activators. The use of kaolin as additive in bamboo combustion as energy source was to prevent the occurrence of sintering/slagging caused by alkali in biomass ash (Llorente et al. 2008) and produced co-combustion residuals containing high silica and high alumina (Purbasari et al. 2016). The resistance of geopolymer mortars to sulfuric acid solution as the most common cause of acid corrosion was investigated. The investigation comprised visual appearances changes, mass changes, compressive strength changes, and microstructure changes. The results of this study would be beneficial for the utilization of co-combustion residuals of bamboo and kaolin as geopolymer raw material for Portland cement substitute.

**EXPERIMENTAL**

Materials used in this study were bamboo (*Gigantochloa apus*), commercial kaolin powder, river sand, commercial potassium hydroxide flakes (purity of 90%), commercial sodium silicate solution

(SiO<sub>2</sub>=30%, Na<sub>2</sub>O=9%, H<sub>2</sub>O=61%), and sulfuric acid solution p.a. (purity of 95-97%).

Mixture of bamboo and kaolin with weight ratio of 95:5 was combusted first in fixed bed furnace and then in electric furnace at 550 °C for 3 hours. Co-combustion residuals of bamboo and kaolin contained oxides as presented in **Table 1** from X-ray fluorescence analysis.

**Table 1.** Oxide composition of co-combustion residuals of bamboo and kaolin

Oxide	Wt%
SiO <sub>2</sub>	50.66
Al <sub>2</sub> O <sub>3</sub>	30.98
Fe <sub>2</sub> O <sub>3</sub>	0.98
CaO	0.56
MgO	1.12
K <sub>2</sub> O	11.37
Na <sub>2</sub> O	0.08
TiO <sub>2</sub>	0.15
P <sub>2</sub> O <sub>5</sub>	1.86
SO <sub>3</sub>	1.91
Other	0.33

Geopolymer mortars were prepared from co-combustion residuals, alkaline activators, and river sand. Co-combustion residuals were sieved with 100 mesh standard sieve, while river sand with 16 standard sieve first. Alkaline activator used was mixture of 10 N potassium hydroxide solution and sodium silicate solution with weight ratio of 1:2. The weight ratio of alkaline activator to co-combustion residuals was 1.3:1 and weight ratio of sand to co-combustion residuals was 2.75:1. Liquid materials were mixed with solid materials and stirred for 6 minutes. The mixture was poured into 5 x 5 x 5 cm cubic moulds and cured in moulds for 24 hours.

After geopolymer mortars were removed from the moulds, geopolymer mortars cured in oven at 60 °C for 8 hours and then at room temperature for 28 days. Mortars from ordinary Portland cement (OPC) as control mortars were prepared from commercial OPC, water, and river sand. The weight ratio of water to OPC was 0.485:1 and weight ratio of sand to OPC was 2.75:1 (ASTM C109M 2007). OPC mortars were cured in water for 28 days.

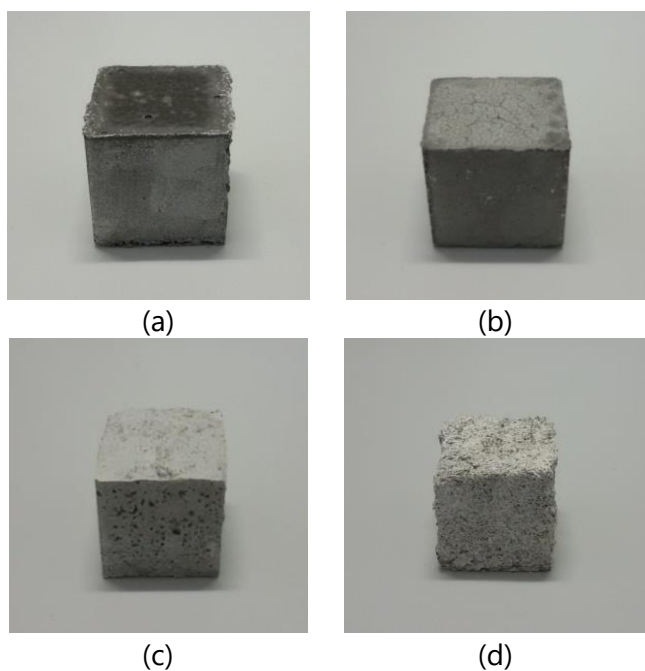
Geopolymer mortars and OPC mortars were immersed in 5% sulfuric acid solution separately for 2, 4, and 6 weeks, respectively. This acid environment is similar to condition in sewage pipes, mining, and food processing industries (Bakharev 2005). Visual appearance, mass, compressive strength, and microstructure were observed on specimens before and after immersion in acid solution. The compressive strength tests were conducted by Ibertest universal testing machine. Fourier transform infrared (FTIR) spectra were collected by the KBr pellet technique using Shimadzu IR Prestige-21 FTIR spectrophotometer. X-ray diffraction (XRD) patterns recorded using Bruker D8 Advance X-ray diffractometer at room temperature under following conditions: 40 kV, 35 mA, and CuK $\alpha$  radiation. Scanning electron microscopy (SEM) images were obtained from gold coated specimens using FEI Quanta FEG 450 scanning electron microscope with 100x magnification.

## RESULTS AND DISCUSSION

### Visual Appearance Changes

Visual appearances of geopolymer mortar before and after immersion in acid

solution for 6 weeks are shown in **Fig. 1(a)** and **1(b)**. There is no significant change in appearance of geopolymer mortars. Geopolymer mortar seems to be slightly deteriorated at the surface and around the edges of specimen. Meanwhile, there is significant change in visual appearances of OPC mortar before and after immersion in acid solution as shown in **Fig. 1(c)** and **1(d)**. The surface of OPC mortar experienced severe deterioration caused by acid solution erosion.

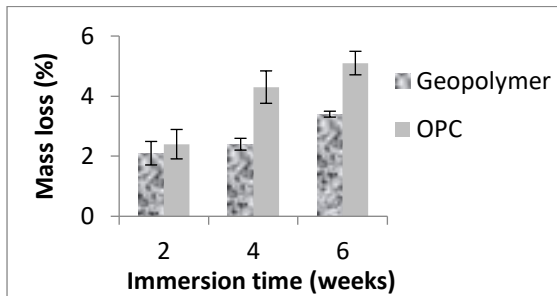


**Fig. 1:** Photographs of (a) geopolymer mortar before immersion in acid solution, (b) geopolymer mortar after immersion in acid solution, (c) OPC mortar before immersion in acid solution, and (d) OPC mortar after immersion in acid solution

### Mass Changes

Mass loss of geopolymer mortars and OPC mortars after immersion in acid solution is shown in **Fig. 2**. Both geopolymer mortars and OPC mortars experienced increase of mass loss along with increase of immersion time in acid

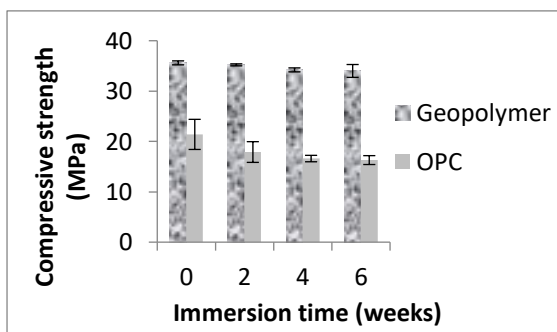
solution. Mass loss of geopolymer mortar after immersion in acid solution for 6 weeks was  $3.4 \pm 0.1\%$ , while mass loss of OPC mortar was  $5.1 \pm 0.4\%$ . These results correspond to visual appearance of OPC mortar that seems more deteriorated than geopolymer mortar.



**Fig. 2:** Mass loss of geopolymer mortars and OPC mortars after immersion in acid solution

### Compressive Strength Changes

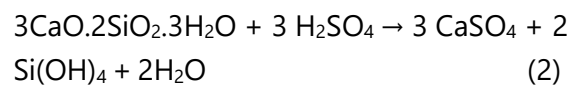
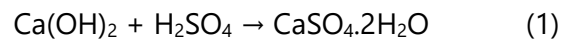
The compressive strength of geopolymer mortar decreased from  $35.6 \pm 0.4$  MPa to  $34 \pm 1.3$  MPa after immersion in acid solution for 6 weeks as shown in **Fig. 3**. The decrease of geopolymer mortar compressive strength by 4.5% was lower than the decrease of OPC mortar compressive strength by 23.8%, i.e. from  $21.4 \pm 2.9$  MPa to  $16.3 \pm 0.9$  MPa. These results suggest that geopolymer mortar has better acid resistance than OPC mortar.



**Fig. 3:** Compressive strength of geopolymer mortars and OPC mortars before and after immersion in acid solution

Geopolymer has empirical formula of  $M_n(-(\text{SiO}_2)_z-\text{AlO}_2)_n \cdot w\text{H}_2\text{O}$ , where: M = cation  $\text{Na}^+/\text{K}^+$ ;  $z = 1, 2, 3$ ;  $n =$  degree of polycondensation (Davidovits 2008). Interaction of geopolymer mortar with acid solution can exchange Na and K ions in geopolymer by hydrogen ion in acid solution. This may be followed by acid attack on Si-O-Al bonds resulting release of aluminium ion and silicic acid. Silicic acid can be polymerized to form amorphous silica on geopolymer surface, while aluminium ion dissolved from geopolymer surface to acid solution. This process can cause mass loss and compressive strength decrease of geopolymer (Bakharev 2005).

Meanwhile, interaction of OPC mortar with acid solution can attack portlandite ( $\text{Ca}(\text{OH})_2$ ) and also decompose C-S-H (calcium silicate hydrate) in OPC to form gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) with following reaction (Allahverdi and Skvara 2000a):

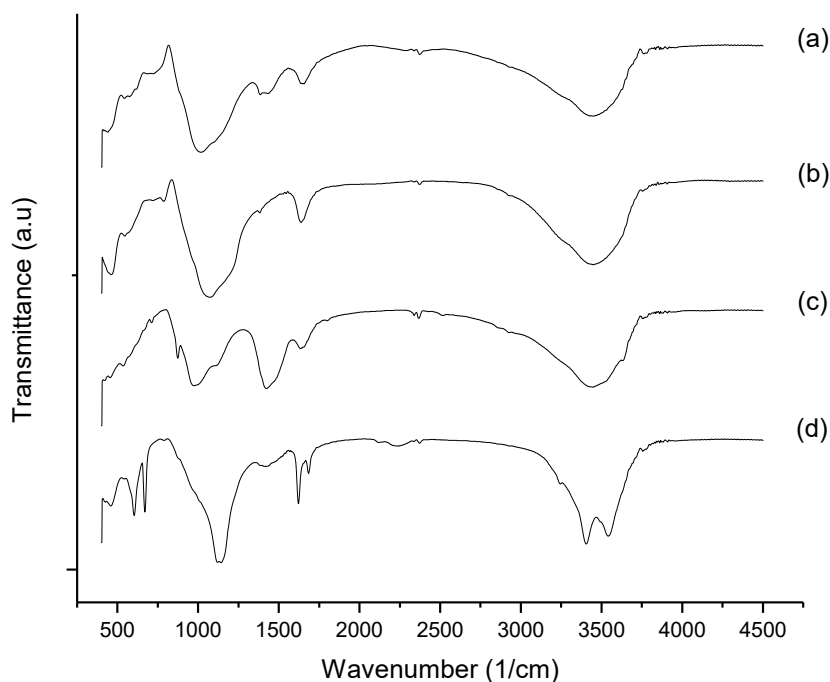


Formation of gypsum takes place rapidly causing deterioration of OPC mortar (Bakharev 2005). Gypsum may remain on OPC surface and extensive deposition of gypsum can cause disintegrating mechanical stresses which leading to cracking (Allahverdi and Skvara 2000b).

### Microstructure Changes

#### FTIR Analysis

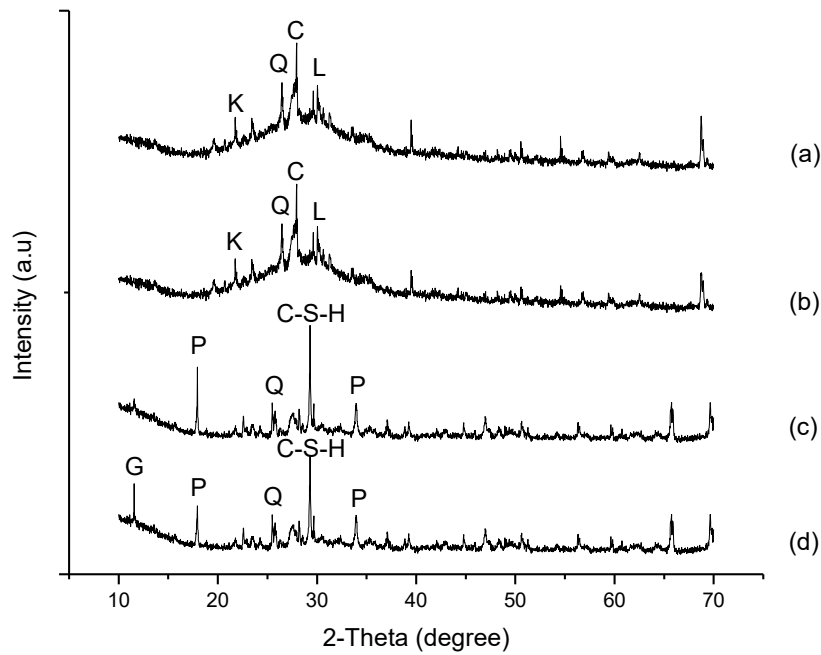
FTIR spectra of geopolymer mortar before and after immersion in acid solution for 6 weeks are shown in **Fig. 4(a)** and **4(b)**.



**Fig. 4:** FTIR spectra of (a) geopolymer mortar before immersion in acid solution, (b) geopolymer mortar after immersion in acid solution, (c) OPC mortar before immersion in acid solution, and (d) OPC mortar after immersion in acid solution

There were several peak shifts, i.e. the Si-O in-plane bending vibration at  $441\text{ cm}^{-1}$  shifted to  $460\text{ cm}^{-1}$ , the Si-O symmetrically stretching vibration at  $723\text{ cm}^{-1}$  shifted to  $786\text{ cm}^{-1}$ , and the Si(Al)-O asymmetrical vibration at  $1018\text{ cm}^{-1}$  shifted to  $1072\text{ cm}^{-1}$ , respectively. These results were similar to those obtained by Bakharev (2005). Peaks at  $1637\text{ cm}^{-1}$  and  $3450\text{ cm}^{-1}$  from adsorbed atmospheric water (Febrero et al. 2015) did not change in geopolymer mortar before and after immersion in acid solution. Peak from carbonate group which was the result of reaction between alkali hydroxide and atmospheric  $\text{CO}_2$  at  $1384\text{ cm}^{-1}$  (Lee and van Deventer 2002) disappeared in geopolymer mortar after immersion in acid solution due to dissolution of carbonate in acid solution (Bouguermouh et al. 2017).

FTIR spectra of OPC mortar before and after immersion in acid solution in **Fig. 4(c)** and **4(d)** also show several peak shifts. Peak from C-S-H (calcium silicate hydrate) at  $972\text{ cm}^{-1}$  (Govindarajan and Gopalakrishnan 2011) shifted to  $1141\text{ cm}^{-1}$  which indicated to the presence of gypsum (Chukanov 2014). Peaks from adsorbed atmospheric water at  $1635\text{ cm}^{-1}$  shifted to  $1622\text{ cm}^{-1}$  and  $1683\text{ cm}^{-1}$ , and at  $3446\text{ cm}^{-1}$  shifted to  $3404\text{ cm}^{-1}$  and  $3543\text{ cm}^{-1}$  which were contributed by the presence of gypsum (Chukanov 2014). New peaks at  $601\text{ cm}^{-1}$  and  $669\text{ cm}^{-1}$  also indicated gypsum formation (Chukanov 2014) in OPC mortar after immersion in acid solution. The similar results were also obtained by Ariffin et al. (2013). Furthermore, peak of carbonate group at  $1423\text{ cm}^{-1}$  disappeared in OPC



**Fig. 5:** XRD patterns of (a) geopolymer mortar before immersion in acid solution, (b) geopolymer mortar after immersion in acid solution, (c) OPC mortar before immersion in acid solution, and (d) OPC mortar after immersion in acid solution (C=chabazite, C-S-H=calcium silicate hydrate, G=gypsum, K=kalsilite, L=leucite, P=portlandite, Q=quartz)

mortar after immersion in acid solution as the case in geopolymer mortar.

**XRD Analysis**

XRD patterns in **Fig. 5(a)** and **5(b)** show that mineral content in geopolymer mortar before and after immersion in acid solution for 6 weeks is unchanged, i.e. chabazite ( $K(AlSi_2O_6) \cdot 3H_2O$ ), kalsilite ( $KAlSiO_4$ ), leucite ( $KAlSi_2O_6$ ), and quartz ( $SiO_2$ ). Chabazite, kalsilite, and leucite are minerals that have silico-aluminate framework and commonly encountered in geopolymer (Davidovits 2008).

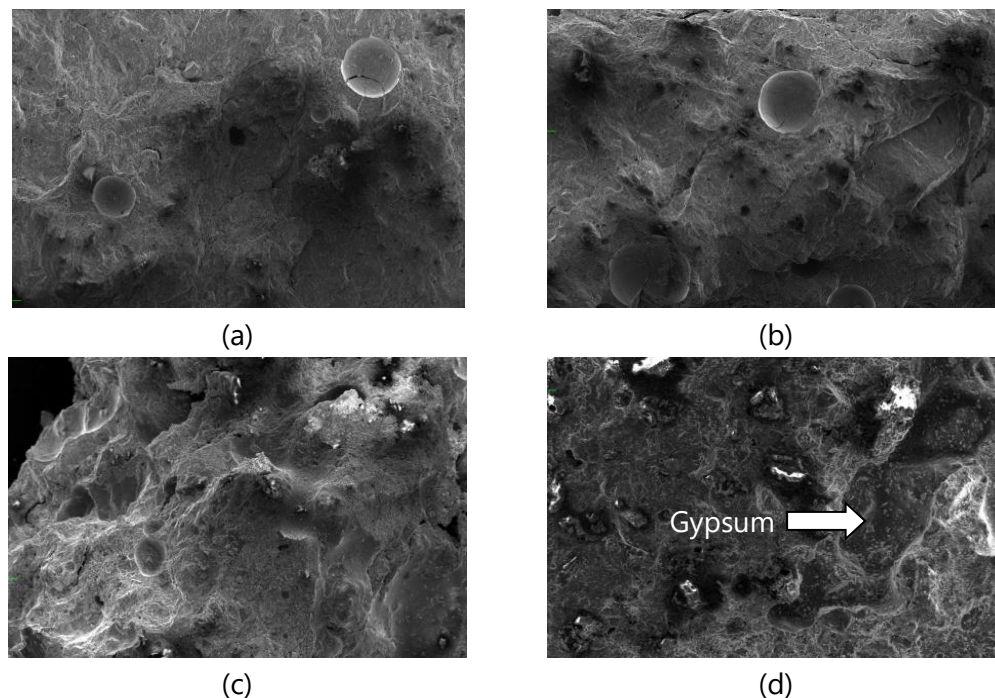
Mineral content in OPC mortars before and after immersion in acid solution seems changed as shown in **Fig. 5(c)** and **5(d)**. OPC mortar before immersion in acid

solution contained C-S-H (calcium silicate hydrate), portlandite ( $Ca(OH)_2$ ), and quartz ( $SiO_2$ ). After immersion in acid solution, gypsum ( $CaSO_4 \cdot 2H_2O$ ) was found in OPC mortar. This result was in accordance with FTIR analysis result.

**SEM Analysis**

SEM images of geopolymer mortar before and after immersion in acid solution for 6 weeks are shown in **Fig. 6(a)** and **6(b)**. The surface of geopolymer mortar after immersion appears more porous than that of geopolymer mortar before immersion in acid solution due to dissolution of aluminium ion and silicic acid.

OPC mortar after immersion also appears more porous and has a lot of



**Fig. 6:** SEM images of (a) geopolymer mortar before immersion in acid solution, (b) geopolymer mortar after immersion in acid solution, (c) OPC mortar before immersion in acid solution, and (d) OPC mortar after immersion in acid solution

fissures compared to OPC mortar before immersion in acid solution as shown in **Fig. 6(c)** and **6(d)**. This indicates that surface of OPC mortar suffered more sulfuric acid solution attack than surface of geopolymer mortar. The presence of new crystal (gypsum) is also seen on OPC mortar after immersion in acid solution.

## CONCLUSIONS

The resistance of geopolymer mortars from co-combustion residuals of bamboo and kaolin to 5% sulfuric acid solution were studied for up to 6 weeks. Visual appearance of geopolymer mortar after immersion in acid solution seemed not changed, while OPC mortar seemed deteriorated severely. Mass loss and

compressive strength loss of geopolymer mortars were lower than those of OPC mortars. FTIR spectra, XRD patterns, and SEM images revealed gypsum formation in OPC mortar after immersion in acid solution. The results confirmed that geopolymer mortars were more durable in the acid environment compared to OPC mortars.

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