Original Article

Deterioration in the microstructure of metakaolin-based geopolymers in marine environment

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\textbf{A B S T R A C T}

In this research, metakaolin-based geopolymers were synthesized to study their deterioration in marine environment. The geopolymers were exposed in air, seawater, dry-wet and heat-cool cycles of seawater for 30, 60 and 90 days. The mechanical property of the geopolymers was characterized through compressive strength measurements, and their microstructures were measured by X-ray diffraction (XRD), scanning electron microscope (SEM) and nuclear magnetic resonance (NMR) apparatus. It was found that seawater environment inhibited the geopolymerization reactions, so that a low amount of tetrahedral silicon of Q\textsuperscript{4}(4Al), Q\textsuperscript{3}(3Al) and Q\textsuperscript{2}(2Al) were formed.

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1. Introduction

Concrete of coastal and offshore structures that exposes in seawater with dry-wet and heat-cool cycles has to endure complicated chemical attack from corrosive ions such as Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−} and Mg\textsuperscript{2+} [1,2]. For ordinary Portland cement (OPC) concrete, corrosive ions can react with the hydration products, namely calcium silicate hydrate (CSH) and calcium hydroxide Ca(OH)\textsubscript{2}, forming Friedel’s salt, ettringite, brucite, magnesium silicate hydrate, etc. [3]. The precipitation and crystallization of these salts in pores of the OPC concrete, which are accelerated by the dry-wet and heat-cool cycles, lead to the formation of cracks and corrosion [4,5]. Therefore, special concrete with high resistance to marine environment is studied extensively [6–8]. In recent years, some researchers explored geopolymers to serve as high anticorrosion concrete for marine structures [9–12]. Geopolymers are alkaline- or alkali-silicate-activated aluminosilicate binders with three dimensional (3D) amorphous microstructures [13]. The compact tetrahedral silica and aluminum structure of geopolymers may give this concrete protection from intrusion of corrosive ions in marine environment [14]. For example, it was reported that chloride diffusion coefficient in fly ash-based geopolymers was half
of that in OPC concrete [15]. Skvara et al. immersed a fly ash-based geopolymer into 44 g/L Na2SO4 or 5 g/L MgSO4 solutions for 720 days, and found that the mass and dimension of the geopolymers kept constant [16]. Zhang et al. prepared metakaolin-based geopolymers to serve as protection coatings for OPC concrete in marine environment. The geopolymer concrete showed low permeability (permeability coefficient around $10^{-6} \text{ m}^2$) and high anticorrosion property against seawater, which were attributed to their low porosity (22.3%) and small open pores (<20 nm) [17,18]. A fly ash-based geopolymer concrete was prepared, cured in air for 28 days and then exposed in tidal zone of marine environment for 3 years, of which the compressive strength increased slightly, low chloride intrusion and steel corrosion were observed [19]. These studies provide clues for the anticorrosion of geopolymers from intrusive ions in marine environment. However, explanations of the anticorrosion properties were based onambiguous and indirect evidences. For example, low permeability was used to verify their ability from chloride intrusion [19]. There is lack of study on the evolution of tetrahedral silica and aluminum structures in geopolymer under marine environment with dry-wet and heat-cool cycles.

The present work used geothermal clay which is rich in kaolinite to synthesize a metakaolin-based geopolymer. It studied the evolution in microstructure of the geopolymer when they were cured in artificial seawater under dry-wet and heat-cool cycles of 30, 60 and 90 days. The geothermal clay is an industrial waste produced in geothermal energy exploitation, which was reported in the synthesis of metakaolin-based geopolymers elsewhere [20].

## 2. Experimental

### 2.1. Materials

Geothermal clay rock was collected from the Los Azufres geothermal field, Mexico at the depth of 250 m where the temperature exceeds 150 °C. The rock was crushed and ground into powder with the $d_{50}$ and $d_{85}$ values of 13.0 and 27.4 μm, respectively, measured from a Beckman Coulter (USA) particle size analyzer. Table 1 gives the chemical analysis of the geothermal clay measured by an X-ray fluorescence (XRF, PANalytical Axios, Holland). SiO2 and Al2O3 are the main components, and the Si/Al ratio is around 3.7:1. X-ray diffraction (XRD, Bruker D8, Germany) pattern of the geothermal clay (Fig. 1) shows main components of kaolinite and cristobalite. The geothermal clay was calcined at 800 °C for 6 h to prepare metakaolin. Sodium silicate (Na2SiO3) and sodium hydroxide (NaOH) with reagent grade ACS were purchased from Sigma-Aldrich and used as alkali activator in the syntheses. Distilled water was used for the synthesis, while artificial seawater was prepared for the exposure of geopolymers. The seawater in 10-fold concentration was prepared with 292.5 g/L NaCl, 7.45 g/L KCl, 36 g/L MgSO4, and this seawater was renewed every 7 days during the curing process.

### 2.2. Methods

In syntheses of the geopolymers, 0.25 molar NaOH, 0.5 molar Na2SiO3 and 12 molar water (H2O) were first mixed to prepare the alkaline solution, then 222 g calcined geothermal clay was added into the alkaline solution and agitated for 5 min. The Si/Al, Na/Al and solid to liquid ratios in the syntheses were 3:7:1, 1.8:1 and 1:4:1, respectively. Next, the mixture was cast into cubic steel molds (50 mm × 50 mm × 50 mm), which were vibrated on a vibration table for 3 min to liberate the air bubbles. After that, the samples were sealed and cured at 60 °C for 6 h and room temperature for 7 days to obtain the initial geopolymer.

The obtained metakaolin-based geopolymers were further exposed under four types of conditions. They were (1) in air, where the geopolymer samples were exposed in air at room temperature; (2) in seawater, where the geopolymer samples were exposed under seawater; (3) in dry-wet seawater cycle, where the geopolymer samples were exposed under the cycle of 12 h in air (25 ± 2 °C) and 12 h in artificial seawater (25 ± 2 °C); (4) in heat-cool seawater cycle, where the geopolymer samples were exposed under the cycle of 12 h in freezer (−15 ± 2 °C) and 12 h in seawater (25 ± 2 °C). For each condition, the geopolymer was exposed for 30, 60 and 90 days, and then the mechanical property and microstructure were characterized.

Compressive strength of the geopolymers was measured with an EHC-1300 mechanical tester from Xingao Technology, China. In each measurement, three specimens were tested and the average value was given. Scanning electron microscope (SEM) of JEOL JSM-5610LV, Japan was used to characterize the microstructure of the geopolymers. X-ray diffraction (XRD) patterns of the geopolymers were obtained by a Brucker D8, Germany diffraction meter, using monochromatic Cu-Kα1 radiation ($\lambda = 1.5406 \text{ Å}$). 29Si nuclear magnetic

### Table 1 – Chemical analysis of the geothermal clay.

<table>
<thead>
<tr>
<th>Components</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>SO3</th>
<th>K2O</th>
<th>Fe2O3</th>
<th>P2O5</th>
<th>TiO2</th>
<th>ZrO2</th>
<th>CaO</th>
<th>CuO</th>
<th>Na2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (%)</td>
<td>67.2</td>
<td>15.5</td>
<td>7.25</td>
<td>7.15</td>
<td>1.18</td>
<td>1.16</td>
<td>0.31</td>
<td>0.19</td>
<td>0.04</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

![Fig. 1 - XRD pattern of the geothermal clay.](image-url)
Fig. 2 – Compressive strengths of the metakaolin-based geopolymers exposed differently.

 resonance (NMR) spectra of the geopolymers were obtained by using the NMR spectroscopy (Bruker AVANCE III) at 79.49 MHz. Powdered binder specimens were packed into 7 mm ZrO2 rotors. Spectra were acquired at spinning speeds of 5 kHz with peak positions referenced to an external standard of tetramethylsilane (TMS) and recorded with 5 s delay time. The excitation pulse for 29Si was 6/262 s with a recycle time of 5 s.

3. Results and discussion

Fig. 2 gives the compressive strength of the geopolymers exposed in various conditions. The initial geopolymers cured at 7 days had a compressive strength of 48.7 MPa. For the exposure in air, the compressive strength increased steadily to 54.5, 58.4 and 59.4 MPa at 30, 60 and 90 days, respectively. Such a high compressive strength suggests that metakaolin obtained through the calcination of geothermal clay has a high activity in the geopolymerization reactions [20,21]. For the exposure in seawater, the compressive strength decreased significantly to 32.1 MPa at 30 days, which may be attributed to the dilution effect of seawater in geopolymerization reactions [17,22–24]. Then it increased slightly to 33.6 and 35.0 MPa at 60 and 90 days, respectively, indicating the slow rate of geopolymerization reactions in seawater. For the exposure in dry-wet cycle, compressive strength of the geopolymers decreased steadily to 43.3, 41.4 and 38.9 MPa at 30, 60 and 90 days, respectively. For the exposure in heat-cool cycle, the compressive strength decreased more than that in dry-wet cycle, which was eventually of 33.1 MPa at 90 days. The compressive strengths of dry-wet and heat-cool cycles suggest the deterioration in mechanical properties of the metakaolin-based geopolymers in simulated marine conditions, which is in agreement with the report of OPC concrete [25].

Fig. 3 shows the SEM images of the geopolymers exposed in air, seawater, dry-wet and heat-cool cycles for 90 days. All the geopolymers show homogeneous binder structures, suggesting the seawater environment only influence the formation of metakaolin-based geopolymers moderately. However, halite precipitation is observed on the geopolymer exposed in

Fig. 3 – SEM images of the geopolymers exposed differently for 90 days.
seawater. The geopolymer exposed in dry-wet cycle shows small cracks along the cristobalite particle, and the geopolymer exposed in heat-cool cycle shows larger cracks in binder. The precipitation of halite and the formation of cracks may be the reasons for the lower compressive strengths of the geopolymers (Fig. 2).

Fig. 4 presents the XRD patterns of the geopolymers exposed in air, seawater, dry-wet and heat-cool cycles of seawater for 90 days, in which the XRD pattern of the initial geopolymer is given as a comparison. The hump of geopolymer gel centered at approximately 27°–29° 2θ is featureless for these geopolymers, which may be attributed to the noise of high cristobalite content in the geothermal clay. The cristobalite and the trona are observed in the initial geopolymer. The cristobalite in the raw geothermal clay maintain after 90-days exposure in the four types of conditions, indicating its inert property in geopolymerization reactions. The formation of trona is attributed to the high alkali concentration and carbonation in the syntheses. It therefore disappears after exposure under seawater, dry-wet and heat-cool cycles of seawater, because of the dilution of the alkali by the seawater. However, halite is observed in the exposure conditions with seawater, which is in good agreement with SEM images (Fig. 3). It indicates that substantial salts are formed when the geopolymers were exposed in seawater.

The $^{29}$Si nuclear magnetic resonance (NMR) spectra had found great success in studying the microstructures of geopolymers, particularly their short-range ordering and molecular structure [26]. The lack of spectral resolution for silicon has been overcome by adopting Gaussian peak deconvolution to separate and quantify Q$^m$(mAl) species ($0 \leq m \leq n \leq 4, m, n=$ integer) [27]. In the geopolymer gel, it has been reported that all silicon and aluminum sites are in tetrahedral coordination, thus $n = 4$ [28–30]. And the resonance of a Q$^4$(mAl) center with the replacement of each aluminum by silicon is an approximate $-5$ ppm difference in $\delta$, with Q$^4$(4Al), Q$^3$(3Al), Q$^2$(2Al), Q$^1$(1Al) and Q$^0$(0Al) resonating at approximately $-84, -89, -93, -99$ and $-108$ ppm, respectively [27]. Fig. 5 gives the $^{29}$Si NMR spectra and the deconvolution of the geopolymers exposed differently for 30, 60 and 90 days,
in which the spectrum of the initial geopolymer is given as a comparison. The spectra not only show a broad peak of geopolymer gel, but also show sub-peaks that represent the formation of silicate derivatives. These silicate derivatives show structures of single tetrahedral structure from the monosilicates (Q0) to the end groups (Q1), to the chain middle groups (Q2), to the layers and the branching sites (Q3), and finally to the three-dimensional networks (Q4). Here the resonances of Q1, Q2 and Q3 resonate at approximately −79, −85 and −95 ppm, respectively, and the resonance of Q4 is the same as the Q4(0Al) of the geopolymer gel [31]. In addition, the peak with resonance at −112 ppm is attributed to the remained cristobalite in the geopolymers [32]. After deconvolution, all units of the species are shown by bars in the bottom of Fig. 5. The bars are centered at the deconvoluted peaks of the species, and their lengths represent the widths of the peaks.

Fig. 5 shows the main peak of the geopolymer gel is centered at δ of −91 ppm for the initial geopolymer, while that for the geopolymers exposed for a period of days is centered at a δ less than −91 ppm. Because the Q4(4AI), Q3(3Al), Q2(2AI), Q1(1Al), Q0(0AI) resonate at approximately −84, −89, −93, −99 and −108 ppm, respectively, the lower values in δ suggest the formation of less sites of tetrahedral aluminum linking with the tetrahedral silicon. With considering the high Si/Al ratio of 3.7 in the raw materials, this result suggests that geopolymerization reactions are started with aluminum precursors and last for a long time [30]. However, the geopolymers exposed in seawater have the peaks that are centered at the δ of much lower ppm, than that exposed in air. For example, the geopolymer exposed in heat-cool cycle of seawater for 90 days has the peak centered at the δ of −95 ppm, while that exposed in air is −93 ppm. It indicates that the marine conditions inhibit the geopolymerization reactions.

Based on the deconvolutions of the spectra in Fig. 5, the percentages of each species in the geopolymers are shown in Table 2. In the initial geopolymer, the sum of silicate derivatives (Q1, Q1 and Q3) is 24.1%. As exposing the geopolymers for 30, 60 and 90 days, silicate derivatives are transformed into geopolymer gel. For example, as exposing in air for 90 days, silicate derivatives decrease to 3.8%, while the geopolymer gel increases from 67.5% to 86.5%. It suggests that the geopolymerization reactions proceed for a long time. In addition, the sum of Q4(4AI), Q3(3Al) and Q2(2AI) is 47% for exposing in air of 90 days, while they are 44.6%, 44.8% and 42.3% for exposing in seawater, dry-wet and heat-cool cycles in seawater. It suggests again that the marine conditions inhibit the geopolymerization reactions.

4. Conclusion

1. Compressive strength of metakaolin-based geopolymers increases as exposing in air until to 90 days, while it decreases as exposing in seawater, dry-wet and heat-cool cycles of seawater. Cracks and salts such as halite are formed in the exposure conditions with seawater, leading to the decrease in compressive strength.

2. In the exposure for 90 days, species of silicate derivatives (Q1, Q1 and Q3) transform into geopolymer gel in proceeding the geopolymerization reactions. However, seawater environments inhibit the geopolymerization reactions, resulting in the formation of less amount of geopolymer gel in Q4(4AI), Q3(3Al) and Q2(2AI).

Conflicts of interest

The authors declare no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmrt.2019.03.010.

REFERENCES