Characteristics of geopolymer hybrid concrete in peat water

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Abstract. Geopolymer hybrid is a combination of geopolymer and Ordinary Portland Cement (OPC) or other binders to produce an alternative binder. This type of binder could be used to transform low-quality fly ash into multi-purpose concrete. Ordinary Portland Cement (OPC) concrete subjected to an acidic organic environment such as peatland, is more prone to deterioration in long-term than concrete using the supplementary cementitious material. In this research, the geopolymer was made by activating low-quality fly ash (contains more than 15% carbon) with the alkaline activator. The inclusion of OPC and Portland Cement Composite (PCC) as a fly ash replacement material is intended to promote curing at ambient temperature and immobilization of heavy metals in fly ash. The specimens were cast and cured at ambient temperature up to 28 days. OPC was used as a control mix. Subsequently, the concrete was immersed in fresh peat water in the laboratory up to 28 days. Characteristics of the geopolymer hybrid such as compressive strength, porosity, and leaching were determined. Microstructure analysis, such as SEM-EDX and FTIR, were conducted. Results show that the geopolymer hybrid has a good strength development at early days. At 28 days, there was a reduction of strength and increase of porosity, probably due to the attack of calcium from the OPC concrete. There was a transformation of aluminosilicate gel into C/N-A-S-H that is advantageous for the strength development at the early days. However, a weaker material has formed in the long term that cannot resist further acid attack. It can be concluded that the geopolymer hybrid is a promising binder, but it is essential to design the material appropriately to have better strength, durability and environmental properties in the long term.

1. Introduction

The fast development of geopolymer research as an alternative construction material globally in the last decades still has a problem of its viability in the application. The geopolymer needs a high temperature to accelerate the polymerization process, but it is challenging to use it for cast-in-situ application without suitable equipment [1]. However, Mejia et al. have reported a new type of geopolymer material that had been developed by various researchers to overcome the issue [2]. The geopolymer is known as geopolymer hybrid that combined ordinary geopolymer with other materials
containing calcium such as slag or Ordinary Portland Cement (OPC) to assist ambient temperature curing. The geopolymer hybrid has a low calcium content below 30%, and a high proportion of geopolymer (more than 70%) [3]. Previous studies by Bocullo et al. [4], and Garcia-Lodeiro et al. [5] reported a strength improvement in the geopolymer mixed with the OPC at the ambient temperature curing. Other studies show an increase in compressive strength by 52% at 28 days and reduction of microcracks and porosity by incorporating OPC in geopolymer concrete. The use of OPC helps a faster geopolymer bond and increases the strength at curing room temperature [6, 7].

Riau has the largest peatland area in Indonesia, with approximately 3.9 million hectares [8]. Peat is classified as organic soil with high organic content, high acidity and low bearing capacity [9]. Concrete in the acid environment is prone to deterioration because acid attack causes alteration of microstructure, a reduction of porosity, and subsequent strength in concrete structures. Olivia et al. [10, 11] suggested the inclusion of pozzolanic materials to increase the concrete resistance in the peat environment. In another study, the fly ash geopolymer has the potential to be utilized as a sustainable concrete infrastructure in peatland due to its resistance in peat water [12].

In addition to the harmful acid ions, environmental condition and microorganism presence [13], the heavy metals leaching of the geopolymer to the peatland has still not been understood. Fly ash waste is classified as hazardous and toxic wastes to the peat environment because it contains heavy metals, such as Pb (lead), Cu (copper), Cd (cadmium), Zn (zinc), and Cr (chromium) [14]. Presence of heavy metals in peat water is a matter of great concern, as those metals are hazardous for human being and the environment since the content above the permissible limit of heavy metals in drinking water can be harmful to aquatic life and human. It was discovered that the Ordinary Portland Cement (OPC) in geopolymer was effective to immobilize heavy metals in fly ash. The heavy metals remain physically bonded in the concrete and will not cause environmental pollution in the long term [15].

This study aims to investigate the geopolymer hybrid concrete characteristics after subjected to peat water. The OPC and Portland Composite Cement (PCC) were used as the fly ash replacement material in this research since the OPC is no longer available in the market of certain areas. The geopolymer hybrid characteristics that are determined after subjected to peat water are compressive strength, porosity, leaching and microstructure. The present study will contribute to a broader application of geopolymer hybrid as a construction material in peatland.

2. Materials and methods

The fly ash is originated from Ombilin Steam Power Plant Station, West Sumatera, Indonesia. The material has low quality because it contains more than 15% carbon. Ordinary Portland Cement (OPC) and Portland Composite Cement (PCC) were used to replace fly ash in geopolymer concrete. The aggregates are from Kampar Regency. The fine aggregate has a modulus fineness of 2.94, absorption of 0.20% and the specific gravity of 2.65, while coarse aggregates with the specific gravity of 2.56 and absorption of 1.99%. Chemical composition of the fly ash, OPC and PCC are shown in table 1.

| Table 1. Chemical composition of fly ash, OPC and PCC. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Material        | SiO₂ (%)        | Al₂O₃ (%)       | Fe₂O₃ (%)       | CaO (%)         | MgO (%)         | K₂O (%)         | Na₂O (%)        | P₂O₅ (%)        | SO₃ (%)         | MnO₂ (%)        | LOI (%)         | Others (%)       |
| Fly ash (%)     | 59.25           | 29.25           | 5.45            | 1.54            | 0.31            | 2.23            | 0.68            | 0.04            | 0.29            | 0.01            | 18.89           | 0.83            |
| OPC* (%)        | 20.92           | 5.49            | 3.78            | 65.21           | -               | -               | -               | -               | -               | -               | 4.60            |                |
| PCC* (%)        | 23.04           | 7.40            | 3.36            | 57.38           | 0.63            | -               | 0.52            | -               | 1.78            | -               | -               | 5.89            |

*[16, 17]

| Table 2. Mixture composition of concrete. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Mixture         | Quantity per m³(kg) |
| GP-OPC          | OPC             | PCC             | Fly ash         | Fine agg.       | Coarse agg.     | Water           | NaOH            | Na₂SiO₃       | SP              |
|                 | 76.83           | -               | 435.37          | 546.00          | 1014.00         | 120.00          | 93.66           | 234.15         | 7.68            |
The geopolymer hybrid mixtures were prepared, i.e. the OPC (GP-OPC) and PCC (GP-PCC) to replace fly ash by 15%. The control mix was a plain OPC concrete with a target compressive strength of 20 MPa. The geopolymer hybrid concrete was prepared using fly ash as the main binder, and alkaline activator solutions consisted of 10M sodium hydroxide (NaOH) and sodium silicate (Na₂SiO₃) with 2.50 modulus silicate (Ms). The superplasticizer was Sikament NN with 1.5% of fly ash added to improve the workability of the geopolymer mixture. The complete mixture composition of concrete is shown in table 2.

The geopolymer specimens were made by mixing the dry ingredients such as fly ash, aggregates, OPC and PCC with the alkaline activator. Cylinder specimens with a dimension of 105x210 mm for the compressive strength and 105x105 mm for the porosity tests. The samples were cured in room temperature for 28 days, then immersed in peat water for another 28 days. Meanwhile, the OPC concrete samples were cured in water for 28 days before placed in the peat water for up to 28 days.

The physical and chemical composition of the peat water from Rimbo Panjang, Riau Province are listed in table 3. The test was carried out at Research and Industrial Standardization Agency, Padang, West Sumatra.

### Table 3. Physical and chemical composition of peat water.

| Parameters       | Unit  | Drinking water qualities [18] | Results |
|------------------|-------|------------------------------|---------|
| Color            | TCU   | 15                           | 34.60   |
| Turbidity        | NTU   | 5                            | 15.90   |
| pH value         | -     | 6.5-8.5                      | 5.01    |
| Organic content  | mg/L  | 10                           | 28.38   |
| Alkalinity       | mg/L  | 500                          | 4.59    |
| Iron (Fe)        | mg/L  | 0.3                          | 0.8845  |
| Manganese (Mn)   | mg/L  | 0.40                         | 0.2321  |
| Sulfate (SO₄²⁻)  | mg/L  | 250                          | 68.20   |
| Chloride (Cl)    | mg/L  | 250                          | 2.34    |

Compressive strength and porosity tests were carried out for all mixtures. Change in compressive strength could be calculated from equation (1). A similar principle was used to calculate the change in porosity.

\[
\text{Change in compressive strength} = \left(\frac{S_2-S_1}{S_1}\right) \times 100
\]  

where \(S_1\) = average compressive strength of a set of specimens following the conditioning period (MPa), \(S_2\) = average compressive strength of a set of specimens following the test period (MPa).

Heavy metals from leachate of solid specimens immersed in peat water at 7 and 28 days were determined using AAS (Atomic Absorption Spectrophotometer). The SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-Ray) and FTIR (Fourier Transform Infrared Spectroscopy) analysis were taken to investigate the microstructure and compounds for all samples.
3. Results and discussion

3.1. Compressive strength

Compressive strength change of concrete after immersed to the peat water at 0, 7, 14, and 28 days is presented in figure 1. The compressive strength of OPC (control mix) gradually decreases by 7.7% and 11.5% at 14 and 28 days subjected to peat water, respectively. The behaviour was reported elsewhere [11-13] since the OPC concrete contains more calcium that is prone to degradation after acidic aggressive ions attack in peat water. It is the fact that strength tends to decrease with the increasing of immersion period for the OPC concrete.

On the other hand, GP-OPC and GP-PCC show an increase in initial strength by 13% and 19.6%, respectively at the 14th day. The behaviour indicates a gradual strength development is still ongoing after seven days in peat water. The GP-PCC specimens had the highest strength change than other mixes since the PCC contains less calcium than the OPC that could resist the early attack of peat water. It is also interesting to note that after 14 days, both GP specimens had a slight decline in strength. The strength reduction is about 2.5-3% at the 28th day, which is probably due to microstructure alteration and network transformation that affect the final strength of the specimens. Very specifically, the geopolymer produces aluminosilicate, and the OPC produces Calcium Silicate Hydrate (CSH), and the combination of geopolymer-OPC or geopolymers hybrid produces (C, N)-A-S-H or N-(C)-A-S-H [19, 20]. It seems that during exposure to the peat water, the geopolymer hybrid behaved like the OPC concrete since continuous calcium leaching reduces paste alkalinity, increases paste porosity, and accelerates decay in the specimens. A similar trend of the disappearance of hydration product was observed by Fernandez-Jimenez et al. [3] for geopolymer hybrid subjected to an acid attack.

![Figure 1. Change in compressive strength after immersed in peat water for up to 28 days.](image)

3.2. Porosity

Figure 2 shows a change in the porosity of both OPC and geopolymer hybrid concrete after subjected to peat water in 28 days. When exposed to the acidic environment, generally the OPC concrete shows an increase in paste porosity due to acid attack to the calcium hydroxide or hydration product of OPC. There was a change of porosity about 12% at 28 days showing consistent damage of the cement paste in the peat environment. A similar finding was observed in the previous studies, and it is recommended to increase the resistance of the OPC by reducing calcium content in the cement using pozzolanic materials [11-13].
Figure 2. Change in the porosity of concrete after immersed in peat water for 28 days.

The geopolymer hybrid specimens showed a reduction of porosity after seven days immersed in the peat water. The porosity reduction was about 2.7% and 8.14% for the GP-PCC and GP-OPC, respectively. The decrease in porosity in geopolymer hybrid concrete is produced by the hydration product of OPC and PCC cement that was used as a substitute for most of the fly ash. The continuous hydration process creates C/N-A-S-H polymerization bond, which reduces porosity by significantly filling the pore space [21]. However, the porosity of GP-OPC increased considerably with exposure time, indicating an acid attack on the specimens. As mentioned in the previous study [19], the geopolymer hybrid product contains C-S-H and other secondary hydration products from the OPC that could be leached due to the low pH, left more empty pores and hasten matrix decay. The GP-PCC was more stable than the GP-OPC, with exposure time indicating better resistance due to multiple hydration gels in the mixture to increase the performance of GP-PCC.

3.3. Leaching

Table 4 shows the post-leaching concentrations of five heavy metals namely Pb (lead), Cd (cadmium), Cu (copper), Cr (chromium) and Zn (zinc), elements deemed by the United States Environmental Protection Agency or USEPA [22] and Indonesian Government Regulation No 101/2014 or PP 101/2014 [23] to be toxic. Based on the results, the concentration of all metals was much lower than the permissible limit per USEPA and PP 101/2014 before immersion in peat water. Although those values have increased gradually with the peat water exposure time, however according to PP 101/2014, some values such as Cu, Cr and Zn were still below the thresholds set by the standards. Both Pb and Cd had higher values than the permissible limit of PP 101/2014, possibly due to the original higher content of those metals in the fly ash. The concentrations found for the heavy metals in both geopolymer hybrid concrete was Zn>Pb>Cd>Cu>Cr. The element with the highest level was Zn (zinc) and considered less dangerous than Pb, Cd or Cr from the toxicity point of view. Interestingly, the GP-OPC exhibits a lower concentration of the heavy metals compared to the GP-PCC. The GP-OPC is more effective to immobilize the metals than the GP-PCC in the peat environment.

Table 4. Leaching of fly ash and geopolymer hybrid concrete after immersed in peat water.

| Mix      | Immersion time (days) | Pb    | Cd   | Cu   | Cr   | Zn    |
|----------|-----------------------|-------|------|------|------|-------|
| Fly ash  | -                     | 5.55  | 7.56 | 14.30| 5.22 | 23.10 |
| GP-OPC   | 0                     | 0.396 | 0.114| 0.290| 0.397| 0.582 |
| Mix          | Immersion time (days) | Pb     | Cd     | Cu     | Cr     | Zn     |
|--------------|-----------------------|--------|--------|--------|--------|--------|
| GP-PCC       | 28                    | 0.472  | 0.185  | 0.382  | 0.432  | 0.687  |
|              | 0                     | 0.491  | 0.157  | 0.461  | 0.500  | 0.731  |
|              | 28                    | 0.717  | 0.190  | 0.553  | 0.690  | 0.836  |
| USEPA limit  | [22]                  | 5.0    | 0.50   | -      | 5.0    | 200    |
| PP 101/2014  | [23]                  | 0.50   | 0.15   | 10     | 2.5    | 50     |

3.4. SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-Ray)

SEM micrographs of geopolymer hybrid concrete are shown in figure 3. In figure 3 (a) and figure 3 (b), the micrographs show geopolymer hybrid surface before exposed to peat water contains fully reacted and unreacted fly ash particles. They are still many pores or holes produced by air bubbles, and the pores are well distributed in the geopolymer matrix. It was also found that there were some particles of fly ash that didn’t react in the microstructure. Fly ash is known to have a significant proportion of hollow particles, which increases porosity in the concrete [24].

Micrographs of geopolymer hybrid after immersed in the peat water after 28 days are displayed in figures 3 (c) and figure 3 (d). It can be seen that the gels from the geopolymerization process have formed perfectly. The surface of microstructure contains fewer pores indicating the formation of C/N-A-S-H bonds in the system, although GP-PCC has a rough surface than the GP-OPC concrete.

Table 5 shows the total percentage of weight elements from geopolymer hybrid concrete with EDX tests. The Si and Al elements in geopolymer hybrid concrete are derived from fly ash, element Ca comes from OPC and the Na element comes from the alkaline activator. The O and C are elements derived from geopolymer hybrid concrete reaction. The Ca element content has decreased after immersed in peat water for both geopolymer hybrid concrete, which indicates the Ca (calcium) leaching due to immersed in acidic peat water. However, Si and Al contents continued to increase, which means aluminosilicate gel polymerization process will continue [23]. Other elements such as Na and O in the GP-OPC have increased, while in the GP-PCC has decreased. This occurs because of differences in reactions due to the different composition between OPC and PCC.
Figure 3. Typical SEM micrograph of geopolymer hybrid concrete: (a) GP-OPC before immersed in peat water, (b) GP-PCC before immersed in peat water, (c) GP-OPC after immersed in peat water for 28 days and (d) GP-PCC after immersed in peat water for 28 days.

Table 5. EDX (Energy Dispersive X-Ray) of geopolymer hybrid concrete.

| Sample | Immersion time (days) | Parameters (%) |
|--------|-----------------------|----------------|
|        | Ca  | Si   | Al   | Na   | O    | C    |
| GP-OPC | 0   | 8.50 | 17.50| 5.80 | 4.70 | 46.10| 17.40|
|        | 28  | 6.05 | 18.05| 5.85 | 7.75 | 47.90| 14.40|
| GP-PCC | 0   | 8.70 | 21.23| 5.95 | 3.80 | 50.35| 9.97 |
|        | 28  | 6.90 | 21.75| 7.35 | 2.90 | 48.50| 12.60|

3.5. FTIR (Fourier Transform Infrared Spectroscopy)

Figure 4 shows the results of the geopolymer hybrid OPC and PCC concrete before and after immersed in peat water for 28 days. The difference in wave intensity that occurs between before and after immersed in peat water. There is a weak peak at GP OPC 0 in 1026.17 cm⁻¹ and a sharp peak at GP OPC 28 in 1004.96 cm⁻¹. There is also a soft peak at GP PCC 0 in 1034.85 cm⁻¹ and a sharp peak at GP PCC 28 in 1002.06 cm⁻¹. The peak shows that the aluminosilicate (A-S-H) formation reaction is complete due to the stretching of O-T-O (O-Si-Al-O) bonds to increase the compressive strength of concrete [25-27]. GP PCC concrete has a broad and strong bond than GP OPC concrete.

In figure 4, GP OPC 0 shows a strong peak in 1413.88 cm⁻¹ and a weak peak in 1488.15 cm⁻¹ at OPC GP 28. There is a strong peak in 1451.50 cm⁻¹ at GP PCC 0 and a weak peak in 1479.47 cm⁻¹ at GP PCC 28. This indicates that the reaction of sodium carbonate (Na₂CO₃) compounds weakened although the sodium leaching from alkali activator (NaOH and Na₂SiO₃) occurs to peat water that the polymerization reaction continues well [26]. The sodium will react with carbon dioxide to form sodium carbonate crystals, which make the structure unstable [28]. GP PCC concrete has a weak bond than GP OPC concrete. The other side, there is a weak peak in 2360.97 cm⁻¹ at GP OPC 0, but the strong peak in 2360.01 cm⁻¹ at GP OPC 28. There is also a weak peak in 2360.97 cm⁻¹ at GP OPC 0 and a strong peak in 2360.01 cm⁻¹ at the OPC 28. This indicates that the C-N bond functional group associated with the formation of zeolite structures will increase if the SiO₂/Al₂O₃ ratio is higher [29]. The structure of zeolite will disrupt the reaction because it makes a polymer condensation process that causes a decrease in compressive strength [30].
4. Conclusions
The combination of geopolymers with Ordinary Portland Cement (OPC) or Portland Composite Cement (PCC) can be used to convert low-quality fly ash into a multi-use concrete and immobilize heavy metals in fly ash that are resistant to acidic environments (peat environment). This is evident from the results of testing the compressive strength, porosity, leaching and microstructure analysis using SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-Ray) and FTIR (Fourier Transform Infrared Spectroscopy). The geopolymer hybrid has better characteristics than OPC concrete when subjected to peat water. The compressive strength increased, the porosity decreased, and from microstructure analysis, the formation of geopolymer hybrid product continues to enhance compressive strength and reduce porosity after immersion in peat water. Based on the results, it can be concluded that the geopolymer hybrid is applicable due to better resistance and less pollution in the peat environment.

Acknowledgment
Authors acknowledged the support/funding from Ministry of Research and Higher Education Indonesia under Penelitian DRPM Skim Penelitian Dasar 2019 Contract no. 787/UN.19.5.1.3/PT.01.03/2019.

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Figure 4. FTIR spectra of the geopolymer hybrid concrete after immersed in peat water for 28 days.
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