Workability and mechanical property of metakaolin phosphate acid based geopolymer

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Abstract: Metakaolin and different molarity of H₃PO₄ were used to synthesis metakaolin phosphate acid based geopolymer (PAG) at 45°C and humidity more than 98%. The fluidity of fresh PAG decreases from 15.2 mm to 13.1 mm according to the increasing molarity of H₃PO₄. Initial setting time and final setting time of fresh PAG increases from 21 h to 62 h and 35 h to 87 h with the molarity of H₃PO₄ increase from 6 mol/L to 12 mol/L respectively. PAG is an early strength material, and the highest strength of PAG is 120.7 MPa at 28 day and strength at 7 day is up to 90.8 MPa. Porosity decreases and pore size increases with the increasing molarity of H₃PO₄. Pore size between 50 nm and 100 nm is dominated in PAG. Some cracks was observed in hardened PAG.

1. Introduction
Geopolymer usually synthesized by alkali-activator and metakaolin while some acid was used to synthesize geopolymer too [1-2]. PAG can be obtained by phosphoric acid and metakaolin, and has higher strength and better thermal resistance than alkali-activated geopolymer[3-4].

In recent years, PAG has received considerable attentions. Some studies focused on the effect of curing enviroments. PAG had been synthesized at a temperature of 60°C for 24 h in an oven and then cured at room temperature for some day while other researches focus on Si/P ratio[3,5-7]. But there is little investigation on the affect of the molarity of H₃PO₄ solution on properties of PAG. A stable temperature and humidity curing condition is been need to maintain geopolymerization steady, uniform and accelerated. Synthesize PAG in this curing condition and investigate the workability and mechanical property of PAG should be interesting.

The main objective of this work is to investigate the workability and mechanism properties of PAG synthesized by metakaolin with different molarity of phosphoric acid solutions at 45°C and the humidity more than 98%. The fluidity and setting time of fresh PAG has been obtained, the strength of hardened PAG was invested, microstructure of PAG was analyzed.

2. Materials and experimental methods
Metakaolin provided by Zhumadian tianyu mineral co. LTD. The chemical composition of metakaolin is shown in Table 1. The metakaolin mainly consists of SiO₂ (49.25 wt%), Al₂O₃ (38.56 wt%) and
Fe₂O₃ (1.21 wt%). Phosphoric acid solutions (H₃PO₄ 85%, Hunan Huihong chemical reagent co. LTD) were used to prepare activator in different molar concentrations corresponding to 6 mol/L, 8 mol/L, 10 mol/L and 12 mol/L. Amounts of H₃PO₄ was fixed and distilled water was used as a solvent. Table 2 shows the formulations of PAG samples.

| Compositions | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | TiO | others |
|--------------|------|-------|-------|-----|-----|-----|--------|
| Mass %       | 49.25| 38.56 | 1.21  | 0.36| 0.28| 1.51| 8.83   |

Metakaolin was mixed with series of phosphoric acid solutions (see Table 2) and was stirred in a planetary mortar mixer for 15 minutes at room temperature. Fresh PAG was poured into Ø30 mm×30 mm PP plastic moulds. The samples were vibrated on a vibrating table for 3 minutes and then were cured at 45°C and the humidity more than 98%.

| Samples    | Molarity of H₃PO₄ (mol/L) |
|------------|-------------------------|
| M6         | 6.0                     |
| M8         | 8.0                     |
| M10        | 10.0                    |
| M12        | 12.0                    |

Vicat apparatus was used to measure the initial and final setting time. The mechanical properties of the geopolymers were evaluated by measuring the compressive strength. Six Ø30 mm×30 mm samples were tested for each molarity. The fragments of every sample were collected after the compressive strength test. Fragments of samples M6, M8, M10 and M12 were collected to prepare the test samples for the mercury intrusion porosimetry (MIP) experiments. An MIP instrument (Autopore IV 9500, Micromeritics) was used to measure the pore size distributions. Porosity was evaluated by using the set-time equilibrium (10 s) mode between the pressure limits of 0.69 kPa and 413.40 MPa. Other collected fragments were used for SEM tests.

3. Results and discussion

3.1 Fluidity of PAG

Amounts of phosphoric acid was fixed, and more molarity means less water for M6 to M12. Phosphoric acid solution is a viscous liquid, viscosity is be closely related the molarity of H₃PO₄ and temperature. The temperature was constant and viscosity of different molarity of H₃PO₄ solution was shown in Table 3, samples M12 has the highest viscosity 6.767 MPa.S while samples M6 has the lowest viscosity 3.779 MPa.S. It noticed that fluidity of fresh PAG decrease from 15.2 mm to 13.1 mm with the increasing molarity of H₃PO₄ solution (see Figure 1). It’s due to the different viscosity of H₃PO₄ solution, and the fluidity is low compared with alkali-activated geopolymer.

| Samples | M6 | M8 | M10 | M12 |
|---------|----|----|-----|-----|
| Viscosity (MPa.S) | 3.779 | 4.346 | 5.204 | 6.767 |
| Conductivity (Ω/m) | 0.201 | 0.213 | 0.180 | 0.173 |
3.2 Setting time of PAG

Setting time is shown in Figure 2, initial setting time of M6 is 21 h and final setting time is 35 h. As molarity of H₃PO₄ solution increasing, initial setting time increases to 62 h while final setting time increased to 87 h for M12. PAG need more time in the geopolymerization than alkali activated geopolymer or cement. Phosphoric acid is the medium strong acid. As the concentration increases the hydrogen bonding between the molecules increases. As showed in Table 3, the viscosity of solution increase while the conductivity goes down.

Metakaolin particles are encased in the phosphoric acid and water in the reaction, metakaolin is layered structure. The ability to enter the reaction layer and the ionic concentration is reduced. With the increase of the viscosity of the phosphate solution. The quantity of phosphate molecules that enter into the layers decrease, the concentration of H⁺ reduced. With the reaction, H₂O was generated and dilute the concentration of phosphoric acid in the interlayer and dissociated more hydrogens. Because of the viscosity of the solution decreased with the concentration of the phosphate acid increased. The hydrogen bond leads to the phosphate molecules to enter into a layer of the metakaolin become difficult. So the setting time is long.

3.3 Mechanical properties and microstructures of PAG

In Figure 3, M10 has the highest compressive strength 90.8 MPa at 7 day and 120.7 MPa at 28 day. Figure 3 show that strength increased with increasing molarity of H₃PO₄. For M6, M8, M10 and M12, the strength at 7 day could be up to 65.05%, 70.16%, 74.71% and 76.34% to the strength at 28 day. The strength at 14 day was up to 92.36%, 90.27%, 87.98% and 89.55% to the strength at 28 day. It indicted PAG is an early strength material. It noticed that strength of M12 is lower than that of M10.

In the micrograph with high magnification 5000× (Figure 4), there are cracks distribute in PAG. As the molarity of H₃PO₄ increases, the amounts of cracks decreases. Higher molarity means less water which evaporates and caused cracks during geopolymerization. More water more cracks. M8 and M10 have less crack than M6 and have higher strength. It because M8 and M10 generated more geopolymer gel. It is interesting that M12 has the most cracks. It because that M12 generates more water than other samples during the geopolymerization, water evaporates and causes cracks. There are some bubble in
M6, it indicated excess water.

Figure 3. Compressive strength of hardened geopolymers M6, M8, M10 and M12 at 7 day, 14 day and 28 day

Figure 4. SEM images of hardened geopolymers M6, M8, M10 and M12 at 28day
   a. M6, b. M8, c. M10, d. M12
Porosity are shown in Figure 5, porosity decreases from 19% to 8% with the increasing molarity of H₃PO₄ for M6, M8, M10 while M12 has the 13% porosity which is higher than M10. Porosity Figure 6 show the obtained curve of log differential intrusion curve vs pore diameter. An increase in the pore size of the PAG is observed with increasing molarity of H₃PO₄. This indicates that concentrated pore sizes of M6, M8, M10 and M12 are approximate to 50 nm to 100 nm respectively. Pores in PAG could be transitional pores which exist in between reaction products. This is because porosity is proportional to the amounts of water, M12 generates more water and caused higher porosity than M10. Cracks and porosity decrease the strength.

![Figure 5. Porosity of fresh geopolymers M6, M8, M10 and M12](image1)

![Figure 6. Pore size distribution of geopolymers M6, M8, M10 and M12](image2)

4. Conclusion
The main findings of this study can be summarized as follows:

The fluidity of fresh PAG decrease from 15.2 mm to 13.1 mm, initial setting time increased from 21 h to 62 h while final setting time increase from 35 h to 87 h with the molarity of H₃PO₄ increase from 6 mol/L to 12 mol/L.

Strength of PAG affects by the molarity of H₃PO₄. PAG is an early strength material, strength at 7 day is up to 90.8 MPa, the highest strength of PAG is 120.7 MPa at 28 day according to the 10mol/L molarity.

Pore size of PAG is between 50 nm and 100 nm, and cracks increase with the increasing molarity of H₃PO₄. Pores and cracks reduce the strength of PAG.

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