Experimental study of one-part geopolymer using different alkali sources

Shuntian Ouyang¹²*, Weiquan Chen¹, Zongtang Zhang²³, Xinming Li¹, Wenfeng Zhu¹

¹ Hunan No.6 Engineering Co. Ltd., Changsha, 410015, China;
² Hunan Provincial Key Laboratory of Geotechnical Engineering for Stability Control and Health Monitoring, Hunan University of Science and Technology, Xiangtan, 411201, China;
³ School of Resource and Environment and Safety Engineering, Hunan University of Science and Technology, Xiangtan, 411201, China

* Corresponding author: Shuntian Ouyang, E-mail: shuntian.ouyang@foxmail.com

Abstract. This paper investigates the feasibility of combining different solid alkali materials as activator to prepare one-part geopolymer mortars. The effects of different composite solid activators on aluminosilicate materials were studied and compared with the traditional water glass and sodium hydroxide composite solution activator through the measurement of fresh and harden properties and microstructural analysis. The results showed that sodium metasilicate pentahydrate was more suitable than quick-dissolving sodium silicate for preparation of geopolymer. The addition of sodium carbonate and calcium hydroxide in solid activator enhanced the compressive strength and decreased the setting time and flowability of the mixes. The highest compressive strength (47.4 MPa, 28 d) was obtained with the activators consisting of sodium metasilicate pentahydrate and sodium carbonate. While scanning electron microscope (SEM) analysis indicated that micro-pores left by the dissolution of metasilicate particles might have an adverse effect on the mechanical properties of mortar samples.

1. Introduction

Geopolymer is a cement-free alternative binder with three-dimensional and amorphous network structures synthesised by alkaline activation of aluminosilicate precursors [1], such as metakaolin, fly ash and ground granulated blast furnace slag (GGBFS). Geopolymer has excellent mechanical properties and resistance to the ingress of many deleterious elements, such as chloride and sulphate [2]. Manufacturing of geopolymer consumes about 60% less energy and lead to 60%-80% fewer CO₂ emission than ordinary Portland cement (OPC) [3]. Due to these advantages, geopolymer is considered as a potential alternative to OPC as a sustainable building material. However, the production of geopolymer usually includes the use of alkali activator solution consisting of sodium- or potassium-based silicates, hydroxides or combination of both materials [4], which are corrosive and might cause occupational hazards.

Hence, there has been growing interest among researchers in one-part (“just add water”) geopolymer. In one-part alkali activation, solid activator such as calcium hydroxide, sodium hydroxide, calcium carbonate, or sodium metasilicate are blended with geopolymer precursors like GGBFS, rice husk ash, silica fume, or fly ash, then water is added to initiate the reaction [5]. Although there has been
many studies on the solid alkali activators used in one-part geopolymer, the studies on the combination of different alkali suppliers with different proportions were rarely reported. Besides, it is reported that alkali silicates, the most commonly used alkali activator, are the most expensive and have the highest impact on environment \[6\]. Thus, it is necessary to expand the studies on the use of combination of different kind of alkali sources to explore more effective and efficient methods to initiate reaction of one-part geopolymer.

In this paper, four different solid alkali sources were combined as alkali activators and compared:1) quick-dissolving sodium silicate, 2) sodium metasilicate pentahydrate, 3) sodium carbonate and 4) calcium hydroxide. The solid activator mixed with aluminosilicate precursors consisting of fly ash and GGBFS to prepare one-part geopolymer, and the effects of solid activators were investigated and compared with traditional water glass and sodium hydroxide hybrid activator through assessment of compressive strength, flowability, setting time and microstructure of geopolymer specimens. The aim is to study the effect of combination of different user-friendly alkali suppliers on the fresh and harden properties of geopolymer mortars.

2. Materials and methods

2.1. Materials

The geopolymer precursors consisted of fly ash (obtained from Yueyang, China) and GGBFS (obtained from Yiyang, China), and the oxide compositions and loss of ignition (LOI) of both materials are shown in Table 1. The sodium carbonate with purity of 99% and calcium hydroxide with purity of 95% were supplied by Zhongtai Chemical Co.. Quick-dissolving sodium silicate, sodium metasilicate pentahydrate, and water glass (sodium silicate solution) were supplied by Mingyan Chemical Co., and their chemical compositions and modulus ratio are displayed in Table 2. The aggregate used in this study was ISO standard sand.

2.2. Mix design, mixing and curing

Several series of mortars mixes were synthesised (Table 3). For A1B1 mixes, solid activator was prepared by combining quick-dissolving sodium silicate and sodium carbonate, and in the subsequent series, quick-dissolving sodium silicate was substituted by sodium metasilicate pentahydrate, or sodium carbonate was replaced by calcium hydroxide. Since it has been demonstrated that silicate based activator is the most effective activator for geopolymer\[7\], component B of the solid activator containing sodium carbonate and calcium hydroxide worked as supplementary alkali source for geopolymer, which accounted for 36 kg/m³. A1 and A2 only used quick-dissolving sodium silicate or sodium metasilicate pentahydrate alone as activator for comparison, while M0 as control mixes have

Table 1. The chemical compositions of fly ash and GGBFS

| Oxide            | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | Na₂O | TiO₂ | MgO | K₂O | MnO | SO₃ | LOI a |
|------------------|------|-------|-------|-----|------|------|-----|-----|-----|-----|------|
| Fly ash          | 50.2 | 30.1  | 12.7  | 3.24| 0.44 | 1.27 | -   | -   | -   | -   | 0.29 | 1.22 |
| GGBFS            | 34.8 | 16.3  | -     | 38.5| -    | -    | 4.89| -   | -   | 0.13| 4.83 | 0.55 |

a Loss on ignition

Table 2. The chemical compositions and modulus ratios of different silicate materials

| Material                     | SiO₂ | Na₂O | Modulus ratio |
|------------------------------|------|------|---------------|
| Quick-dissolving sodium silicate | 60.6 | 21.2 | 2.86          |
| Sodium metasilicate pentahydrate | 28.2 | 28.8 | 0.98          |
| Water glass                  | 28.3 | 8.7  | 3.36          |
the common water glass and sodium hydroxide hybrid activator. The target density of mortar is 2065 kg/m³, and the binder content was kept at 33.3% (450 kg/m³). Based on the previous study [8], the fly ash content and GGBFS content accounted for 70% and 30% of binder content respectively. For the liquid alkali activator, the water glass was blended with 10 M sodium hydroxide solution to achieve the desired modulus of 1.4, and the liquid activator was prepared 24 h prior to the mixing.

| Mix   | Fly ash (kg/m³) | GGBFS (kg/m³) | Sand (kg/m³) | Component A (kg/m³) | Component B (kg/m³) | Liquid Activator (kg/m³) | Water (kg/m³) |
|-------|----------------|---------------|--------------|---------------------|---------------------|------------------------|---------------|
| A1B1  | 315            | 135           | 1350         | 72                  | 0                   | 36                     | 0             | 157          |
| A1B2  | 315            | 135           | 1350         | 72                  | 0                   | 0                      | 36            | 0            | 157          |
| A2B1  | 315            | 135           | 1350         | 0                   | 72                  | 36                     | 0             | 157          |
| A2B2  | 315            | 135           | 1350         | 0                   | 72                  | 0                      | 36            | 0            | 157          |
| A1    | 315            | 135           | 1350         | 72                  | 0                   | 0                      | 0             | 193          |
| A2    | 315            | 135           | 1350         | 0                   | 72                  | 0                      | 0             | 193          |
| M0    | 315            | 135           | 1350         | 0                   | 0                   | 0                      | 225           | 40           |

The preparation of specimens was as follows: dry materials were mixed for 3 min, then water or alkali solution (for M0) was added and continued mixing for 3 min. The fresh mortars were cast in 50 mm cube moulds. The cubes were placed in the curing room with set temperature and relative humidity of 20 ℃ and 95% respectively. After 24 h of initial curing, the specimens were demoulded and continued curing for 28 days.

2.3. Test methods
Setting times of fresh mortars were measured with Vicat apparatus in accordance with standard GB/T 1346—2011 [9]. Flowability of fresh mortars were determined with a flow table and a truncated die according to standard GB/T 2419—2005 [10]. Compressive strength was determined with digital compressive machine with loading rate of 2.4 kN/s during the test. The microstructural analysis of geopolymer was conducted through a scanning electron microscope (SEM).

3. Results and discussion
3.1. Compressive strength
The compressive strengths of each mixes at 3, 7 and 28 days are displayed in Fig 1. Depending on the component A of solid activator, it can be seen that mortars using quick-dissolving sodium silicate as component A (A1, A1B1 and A1B2) experienced relatively slow rate of strength growth as compared with their sodium metasilicate pentahydrate counterparts. For A1B1 and A1B2 mixes, their strengths at 28 days were 15.4 MPa and 13.1 MPa respectively, which is the lowest value in the Fig 1. except for A1 mixes. This may be owning to the high SiO₂ content of quick-dissolving sodium silicate, which increased the modulus ratio of solid activator. Conventionally, it has been demonstrated that there is an optimum range of modulus ratio for alkali activator, which around 1-1.5 [11], while the quick-dissolving sodium silicate used in this experiment has a modulus of 2.86, which is outside the optimum range.

Solid activators containing sodium metasilicate pentahydrate were otherwise identical, especially for A2B1 and A2B2 mixes. Both mixes consistently had higher strengths than every mixes else expect for M0, which using alkali solution as activator. It also revealed that sodium metasilicate pentahydrate could attain an acceptable activating effect when paired with sodium carbonate in comparison to calcium hydroxide.
Replacing calcium hydroxide with sodium carbonate as component B of solid activator strengthened the specimens, as A1B1 and A2B1 mixes achieved better performance than A1B2 and A2B2. But increasing the Na₂O content in the geopolymer matrix made the specimens more vulnerable to the influence of efflorescence, which means the alkaline materials react with carbon dioxide and generate white carbonate salt on the surface of specimens.

Using sodium metasilicate pentahydrate alone as activator also had adequate performance, with 34.3 MPa at 28 days, but the most notable point comes from A2B1 mixes, which achieving 47.4 MPa at 28 days, and it is almost equal to the strength of M0 (48.7 MPa). A2B1’s strength growth was pretty slow during the early stage compared with M0 mixes, the strength of A2B1 at 3 days was lower than that of M0 mixes. But the difference between them started to show after 3 days of curing, the strength of A2B1 continually increased fast throughout the period. This might be attributed to that the metasilicate particles were not fully dissolved, leading to a lower water binder ratio compared with design value [12]. As the gradual release of silicate ions within the matrix, the reaction proceeds and strengthens the mortar samples.

Overall, the combination of sodium metasilicate pentahydrate and sodium carbonate had a better performance to the monocomponent sodium metasilicate pentahydrate, and this combination also had a comparable activating effect to the alkali solution, which means it could be easily adapted and efficiently incorporated in the preparation of geopolymer.

3.2. Setting time

Fig 2. presents the initial and final setting times of each mixes. Practically, geopolymer will be no longer workable after the initial setting was exceeded. It was found that the mixes with sodium metasilicate pentahydrate exhibited considerably shorter setting times than their quick-dissolving sodium silicate counterparts. Theoretically, the sodium metasilicate particles dissolved in water, releasing a large amount of heat to precipitate the reaction, which cannot be performed by quick-dissolving sodium silicate. Besides, geopolymersation reaction as an exothermic reaction, the rate of heat generation increases as the rate of reaction increases [13]. The strength comparison mentioned in Section 3.1. also indicates that faster silica availability is one of the core characteristic for high strength growth of geopolymer.

As shown in Fig 2., the setting time of mixes with calcium hydroxide as component B of solid activator were relatively shorter than those of mixes with sodium carbonate. Previous studies reported that the additional soluble calcium supplied by calcium hydroxide reacts with Si and Al to form calcium aluminosilicate hydrate (C-A-S-H) gel, resulting in shorter setting of the mortars [14].

One-part geopolymer has been regularly reported to set relatively quickly resulting from the heat release from the dissolution of particles of activator [15]. The data collected from this study conform to this issue, while A2B1 mixes have the comparable strength to M0 mixes, the setting time were detected 25% shorter than those of M0 mixes.
3.3. Flowability

Fresh mortars were cast in a diameter of 100 mm truncated die and placed on the flow table, then the die was removed to allow mortar to flow freely under the vibration. After 25 times of vibrating, the spread diameter was recorded. The average spread diameters of each mix is shown in Fig 2. For both quick-dissolving sodium silicate and sodium metasilicate pentahydrate mixes, the workability decreased as the sodium carbonate was replaced with calcium hydroxide. The increased resistance of the mortars is probably attributable to the additional calcium ions introduced by calcium hydroxide, which accelerates the reaction and setting process [16]. Consequently, the workability as well as handling time diminished.

It can be seen that the flowability of M0 mixes was the lowest among all the mixtures in Fig 2., with spread diameter of 195 mm. This could be due to the higher viscosity of the liquid activator used in geopolymer. Another possible reason for reduced workability might be the free water added in M0 was 75% lesser than those of solid activator mixes, and the water content is a crucial parameter that affects workability.

3.4. Microstructure

The microstructure of geopolymer matrix was investigated to gain further insight concerning the differences resulting from the use of alkaline sources. Fig 3. depicts the micrographs of specimen intersectons of A1B1, A1B2, A2B1, A2B2 and M0 mixes after 28 days of curing. A1B1 and A1B2 mixes were considerably weaker than other mixes. As seen from the SEM images of A1B1 and A1B2, a large number of fly ash and GGBFS particles remained unreacted, resulting in a less dense matrix. Thus their compressive strengths were rather low at less than 16 MPa at 28 days. However, some partially reacted particle had transformed to inconsistent matrix, which explains the reasons of strength development at later times of curing. A2B1 was the strongest among all mixtures with solid activator. It has a dense microstructure without obvious micro-cracking. The geopolymeric gel had filled the matrix around the unreacted fly ash particles, causing a descend in porosity and pore size of mortar specimens and consequently an intensification in compressive strength. However, the micro-pores left by the dissolution of metasilicate particles were detected in SEM image, which might have a adverse effect on mechanical properties. A2B2 had a rough and uneven microstructure. This might be attributed to the partially developed C-A-S-H gel, hence appeared rougher than A2B1. Besides, it was found that the cracks generated at the interface transition zone (ITZ), which probably lead to strength reduction of specimens. In the sample of M0 control mixes, a dense surface morphology similar to A2B1 was observed. It can be seen from SEM image, the gel was fully developed and distributed evenly in the geopolymeric matrix. This was likely due to the alkaline solution assisted in the
distribution of silica ions through pores, enhancing the overall microstructure. Moreover, the use of liquid alkali activator saved the process of dissolution of alkali particles, preventing the particles from undissolved or partially dissolved, and the geopolymeric product could form shells around the metasilicate particles [12], and the undissolved metasilicate particles were basically equal to air voids into the matrix, which could weaken the strength of specimens.

4. Conclusions
This study aimed to investigate the effects of combination of different user-friendly alkali materials on the fresh and harden properties of geopolymer mortars. From the results of laboratory experiments, the following conclusions could be drawn:

(1) The alkaline sources had a great impact on the geopolymer specimens and large differences in strength development were observed for different combination of solid activators. The activators containing sodium metasilicate pentahydrate outperformed their quick-dissolving sodium silicate counterparts in terms of mechanical properties. The compressive strength of mixes using sodium metasilicate pentahydrate was considerably higher than that of mixes with quick-dissolving sodium silicate.

Fig 3. Scanning electron microscope (SEM) images of different mixes
(2) The addition of sodium carbonate and calcium hydroxide in solid activator improved the strength development and decreased the setting time and workability of one-part geopolymer, especially for mixes with sodium metasilicate pentahydrate. For mixes including calcium hydroxide, the availability of increased C-A-S-H gel was confirmed by SEM images, which attributed to the strength enhancement and shortening of setting time.

(3) The combination of sodium silicate pentahydrate and sodium carbonate (A2B1) achieved the best performance in mechanical properties among all the mixes with solid activators, with 47.4 MPa at 28 days, which is very close to the strength of mixes using liquid activator (48.2 MPa). Nevertheless, the undissolved alkali particles and micro-pores resulting from dissolution of metaslicate particles observed in SEM images might cause reduction in compressive strength to some extent.

Acknowledgements
Authors would like to gratefully acknowledge the support by Hunan Provincial Science and Technology Plan Project (Grant No.: KY201930) and Hunan No.6 Engineering Co. Ltd Science and Innovation Project (Grant No.: LJ50681).

References
[1] Mehta A., Siddique R., 2016. An overview of geopolymers derived from industrial by-products. Construct. Build. Mater. 127, 183–198
[2] Djwantoro H., Wallah S.E., Sumajouw M.J.D., Rangan B.V., 2004. On the development of fly ash-based geopolymer concrete, Aci. Mater. J. 101, 467–471
[3] Tong, K.T., Vinai, R., Soutsos, M.N., 2018. Use of Vietnamese rice husk ash for the production of sodium silicate as the activator for alkali-activated binders. J. Clean. Prod. 201, 272–286
[4] Nikolov A., Rostovsky I., Nugteren H., 2017. Geopolymer materials based on natural zeolite, Case Stud. Constr. Mater. 6, 198–205
[5] Abdollahnejad Z., Pacheco-Torgal F., Aguiar J.B.D., 2015. Development of foam one-part geopolymers with enhanced thermal insulation performance and low carbon dioxide emissions, Adv. Mater. Res. 1129, 565–572
[6] Heath A., Paine K., McManus, M., 2014. Minimising the global warming potential of clay-based geopolymers. J. Clean. Prod. 78, 75–83
[7] Provis J.L., Deventer J.S.J.V., 2014. Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM, vol. 13
[8] Nath P., Sarker P., 2014. Effect of GGBFS on setting, workability and early strength properties of fly ash geopolymer concrete cured in ambient condition, Construct. Build. Mater. 66, 163–171
[9] GB/T 1346-2011, 2011. Test method for water requirement of normal consistency, setting time and soundness of the Portland cement. The Standardization Administration of China, Beijing, China
[10] GB/T 2419-2005, 2005. Test method for fluidity of cement mortar. The Standardization Administration of China, Beijing, China
[11] Wang S.D., Scrivener K.L., Pratt P.L., 1994. Factors affecting the strength of alkali-activated slag, Cem. Concr. Res. 24, 1033–1043
[12] Dong M, Elchalakani M, Karrech A., 2020. Development of high strength one-part geopolymer mortar using sodium metasilicate, Construct. Build. Mater, 236
[13] Luukkonen T, Abdollahnejad Z, Yliniemi J, Kinnunen P., Illikainen M., 2018. One-part alkali-activated materials: a review, Cem. Concr. Res. 103, 21–34
[14] Sun Z., Vollpracht A., 2018. Isothermal calorimetry and in-situ XRD study of the NaOH activated fly ash, metakaolin and slag. Cem. Concr. Res. 103, 110–122
[15] Suwan T., Fan M., 2017. Effect of manufacturing process on the mechanisms and mechanical properties of fly ash-based geopolymer in ambient curing temperature. Mater. Manuf. Process. 32, 461–467
[16] Kumar S., Kumar R., Mehrotra S.P., 2010. Influence of granulated blast furnace slag on the reaction, structure and properties of fly ash based geopolymer. J. Mater. Sci. 45, 607–615