- Technical Paper -

SYNTHESIS OF FA/BFS BASED GEOPOLYMER MORTAR ACTIVATED BY SODIUM METASILICATE NONAHYDRATE

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ABSTRACT

FA/BFS based geopolymer mortar activated by sodium metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) was synthesized. Compressive strength and workability were investigated in terms of the concentration of $Na_2SiO_3 \cdot 9H_2O$, mass ratio of alkaline activator to binder, slag content, mixing time and curing temperature. X-Ray diffraction (XRD) and scanning electron microscopy (SEM) were carried out to identify the reaction products. Results present that $Na_2SiO_3 \cdot 9H_2O$ can be employed in the synthesis of Geopolymer material as a promising alternative to conventional alkaline activator.

Keywords: sodium metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$), GP mortar, mixing time, XRD, SEM

1. INTRODUCTION

Geopolymer synthesis is based on the inorganic alkali activation chemistry. Aluminosilicate rich materials (binders) are activated by using strong alkali solution(activator) to produce an aluminosilicate gel in a three-dimensional polymeric chain and ring structure [1]. Geopolymers have been proved to be green construction materials which can utilize various kinds of industry by-products as their binders. Fly ash (FA) and blast furnace slag (BFS) are the most common ones. Alkaline activators such as sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) are commonly used to activate aluminosilicate materials.

Geopolymerization can be summarized in five steps. (1) Aluminosilicate solids dissolve into the alkaline aqueous phase; (2) the dissolved Al and Si species, and any silicate initially supplied by the activator, interact to form oligomers; (3) the supersaturated system begins precipitation to form gels; (4) geopolymer gel grows and bonds with the residual precursor particles to form a solidified binder; (5) gels continue the transformation to a more ordered state, usually towards zeolite-like phases [2]. It is obvious that both alkaline activator and alkaline binders play important roles in the final reaction products. They are involved in the dissolution of raw materials, break and recombination of the aluminosilicate structure, condensation, polymeric reaction and charge balance in the reaction system [3].

Compared with NaOH, Na_2SiO_3 does much less harm to people. Therefore, it is employed to produce user-friendly geopolymer materials. In this study, sodium metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) was chosen to be alkaline activator. It is a solid powder instead of solution like other activators. This would make handling and casting more simply and conveniently.

Based on trial-and-error pre-experimental results, 18 cases of proportions for geopolymer(GP) mortar were used to investigate the compressive strength, flow and setting time in terms of the concentration of $Na_2SiO_3 \cdot 9H_2O$ (SS/SS+Water, SS%), mass ratio of alkaline activator to binder (SS+Water/BFS+FA, AA/AB), slag content (BFS/BFS+FA, BFS%), mixing time and curing temperature. Furthermore, scanning electron microscopy observation (SEM) and X-ray diffractometer test (XRD) were carried out to identify and analyze the reaction products. The objective of this study is to synthesize FA/BFS based GP mortar activated by $Na_2SiO_3 \cdot 9H_2O$.

2. EXPERIMENTAL DETAILS

2.1 Materials

In order to synthesize GP mortar specimen, fly ash (FA) and blast furnace slag (BFS) were blended as alkaline binder; sodium metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) was used as the alkaline activator. The physical properties and chemical components of the constituent materials were shown in Table 1 and Table 2. According to Table 2, the main oxides in FA were silica and alumina while the main oxides in BS were calcium oxide and silica. In most previous research, Na_2SiO_3 was added into alkaline binder in the form of water glass (liquid) of which concentration was controlled by dilution rate. In practice, it is not easy to handle the water glass because of its high viscosity. In addition, specific delay admixture is necessary during casting because of short setting time. $Na_2SiO_3 \cdot 9H_2O$ is a crystal powder in solid with slow dissolution at ambient temperature. In order to extend the setting time

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Table 1 Physical properties of materials

Materials	Origin and Physical Properties
SS	Na$_2$SiO$_3$ 9H$_2$O, sodium metasilicate nonahydrate produced by Osaka Keisou Corporation, Na$_2$O (wt%): 21.7, SiO$_2$ (wt%): 20.9, molar ratio: Si/Na=1.04
FA	produced by Shinonoda Power Station from The Chugoku Electric Power CO.,INC(JIS A6201-Ⅱ), density: 2.22g/cm^3, specific surface area: 3420cm^2/g.
BFS	produced by Nippon Steel & Sumikin Esment Chubu Corporation (Esment, JIS A 6206 granulated blast furnace slag 4000), density: 2.88 g/cm^3, specific surface area: 4090 cm^2/g.
Sand	Standard sand for the strength test of cement, water absorptivity: 0.42%, bulk density: 1.76kg/L, solid volume percentage: 66.7%
Water	Tap water

Table 2 Chemical components of sand, FA and BFS

Components (%)	ig.loss	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	Na$_2$O	K$_2$O	SO$_3$
Sand	0.00	98.4	0.40	0.40	0.20	0.00	0.10	0.10	---
FA	1.80	64.9	25.2	2.74	1.90	0.97	0.00	1.40	0.51
BFS	0.96	32.3	10.4	0.29	42.2	8.12	0.23	0.41	2.04

Table 3 Proportions of GP Mortar

	Factors of GP mortar					Proportions (kg/m^3)					
Case	SS% (wt%)	AA/AB	BFS% (wt%)	Curing Temperature	Mixing Time (s)	W	SS	FA	BFS	S	Total
1	35	0.50	30	Ambient Temperature 20±0.5℃	330	221	119	476	204	1275	2295
2	30	0.50	30			238	102	476	204	1275	2295
3	40	0.50	30			204	136	476	204	1275	2295
4	45	0.50	30			187	153	476	204	1275	2295
5	35	0.45	30			205	110	490	210	1269	2284
6		0.55				236	127	462	198	1279	2302
7		0.60				250	134	448	192	1280	2304
8		0.50	0			221	119	680	0	1275	2295
9			45			221	119	374	306	1275	2295
10			60			221	119	272	408	1275	2295
11			30		270	221	119	476	204	1275	2295
12			30		390	221	119	476	204	1275	2295
13			30		450	221	119	476	204	1275	2295
14			60		270	221	119	272	408	1275	2295
15			60		390	221	119	272	408	1275	2295
16			60		450	221	119	272	408	1275	2295
17			30	60±0.5℃ for 6h	330	221	119	476	204	1275	2295
18			60			221	119	272	408	1275	2295

, Na$_2$SiO$_3$·9H$_2$O was determined to be an alkaline activator instead of water glass in this research.

2.2 Proportions

In authors' previous work [4], the most dominant influential factors on flow, setting time and compressive strength were discussed of Na$_2$SiO$_3$·9H$_2$O-activated GP mortar by a Taguchi orthogonal experiment program. Based on previous research [5] and the pre-experimental results, 18 cases of mixture proportions were chosen in Table 3. Case 1 was the control one. Case 2, 3 and 4 were used to investigate the influence of sodium silicate concentration (SS%) on the properties of GP mortar; case 5, 6 and 7 were conducted to research the effect of the mass ratio of alkaline activator to alkaline binder ratio (AA/AB); case 8, 9 and 10 were proposed to detect the influence of slag content by mass (BFS%).

Meanwhile, the influence of mixing time on the properties of GP mortar at low slag content (30%) and high slag content (60%) were researched through case 1, 11, 12, 13 and case 10, 14, 15, 16 respectively. Besides, the effect of curing temperature at low slag content (30%) and high slag content (60%) were also investigated through case 1, 17 and case 10, 18 respectively. It was worth mentioning that the water which in the proportions did not include the crystalline water in the Na$_2$SiO$_3$·9H$_2$O. The mass ratio of alkaline mass to sand (SS+Water+FA+BFS/Sand) was kept as 0.8.

2.3 Synthesis and measurements

Since both alkaline binder and activator are in solid, only one-step preparation for mixing the solid materials is necessary. Detailed synthesis follows the following steps: Na$_2$SiO$_3$·9H$_2$O was blended with FA,

BFS and sand in dry condition for 30s; adding water, standing for 30s; mixing with low speed for 30s and then a high speed for 60s; standing for 60s and then mixing with a high speed for 120s. In total, the mixing time was 60s (dry mixing and 1st standing) +30s (low speed) + 60s (1st high speed period) + 60s (2nd standing) + 120s (2nd high speed period) = 330s. Notice that the 2nd high speed period was changed to 60s, 180s and 240s in order to investigate the influence of mixing time as mentioned in 2.2. Consequently, the total mixing time became to 270s, 390s and 450s respectively.

Flow values of fresh mortar were measured according to JIS R5201. Cylinder specimens with 5Φ×10cm were made for measurement of compressive strength. Initial setting time and final setting time were tested according to JIS A1147.

After demolding, the GP mortar specimens were wrapped by plastic film and cured in ambient temperatures of 20±0.5℃ except those for case 17 and 18, which were put into the oven and cured at 60℃ for 6h before in ambient curing temperature. 7d, 14d and 28d compressive strength were tested according to the JIS A1108.

2.4 Results and analysis

Five synthesis factors were considered on their relationships with workability and strength development of GP mortar.

(1) Concentration of sodium metasilicate nonahydrate (SS%)

The effects of SS% on flow, compressive strength and setting time were shown in Fig.1 and Fig.2. With the increase of SS%, the compressive strength increased while the flow and setting time decreased. The reason can be explained as follows. At low SS%, less Si^{4+} and Al^{3+} ions could be dissolved because of low OH^- concentration, resulting in the formation of a weak polymeric network which has lower strength. Meanwhile, an increase of SS% means that less water is added into the mixture, thus leading to lower flow values. Since OH^- ion in activator acts as a catalyst in the chemical reaction and accelerates the dissolution of aluminosilicate species, lower the SS%, lower the reaction rate, consequently longer the setting time for GP mortar.
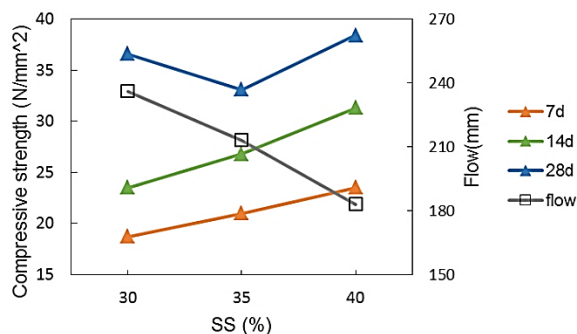

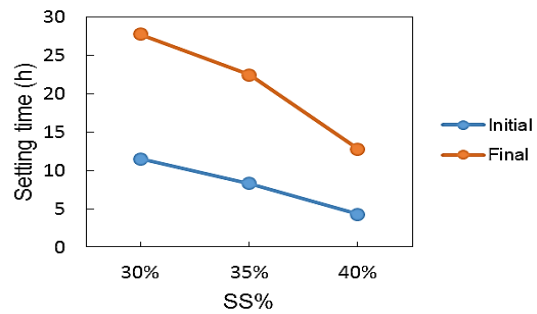Fig.1 Relationship between compressive strength, flow and SS%

Fig.2 Relationship between SS% and setting time

(2) Alkaline activator to binder ratio by mass (AA/AB)

The influences of AA/AB on the properties of GP mortar were shown in Fig.3. Unlike the influence of SS%, with the increase of AA/AB, the compressive strength decreased while the flow increased. As shown in Fig.4, the increase of setting time became gentler after exceeding the value 0.5 of AA/AB, especially in terms of final setting time. Notice that AA refers to the sum of $Na_2SiO_3 \cdot 9H_2O$ and added water. Obviously, an increase of AA/AB would lead to an increase of water content which could result in a longer setting time and a growth of porosity which led to the loss of compressive strength.
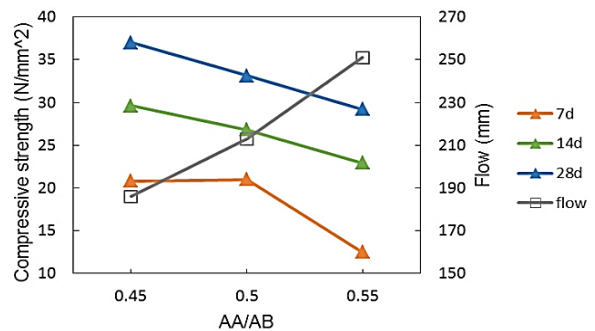

Fig.3 Relationship between compressive strength, flow and AA/AB
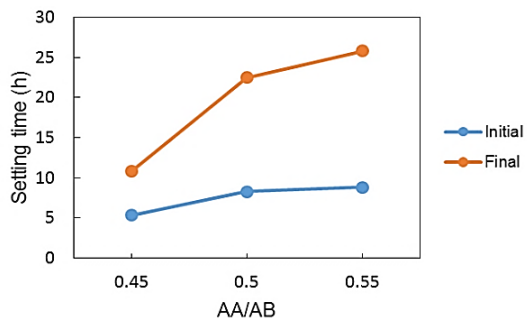

Fig.4 Relationship between AA/AB and setting time

(3) Blast furnace slag content by mass (BFS%)

Fig.5 and Fig.6 show the results of the relationship between BFS% and properties of specimens. It could be seen that higher BFS% resulted in a higher compressive strength. Several plausible explanations were discussed as follows. The inclusion of the BFS would increase the proportion of Si presented in the mixture, correspondingly the ratio of Si/Al, which would determine the relative amount of

AlO$_4$ and SiO$_4$ formed in the geopolymer gel. With the presence of the soluble silicate, higher Si content enhanced the condensation process and introduced more Si in the polymeric chain [6]. This could be beneficial to increase compressive strength. Besides, BFS also introduced CaO into the raw materials. Consequently, hydrated products such as calcium silicate hydrates (C-S-H) along with the alumino-silicate geopolymer network including C-A-S-H would present. They could provide extra compressive strength above FA-based geopolymer materials.

Regarding the change of flow, an increase of BFS% did not influence it significantly according to Fig.5, although the inclusion of irregular particles in slag would reduce the flow value due to the morphological effect.

According to the Fig.6, the setting time decreased gently with the increase of BFS%. This is due to an increase of CaO content which led to a shortened setting time. It is similar to the analysis from previous research [7].
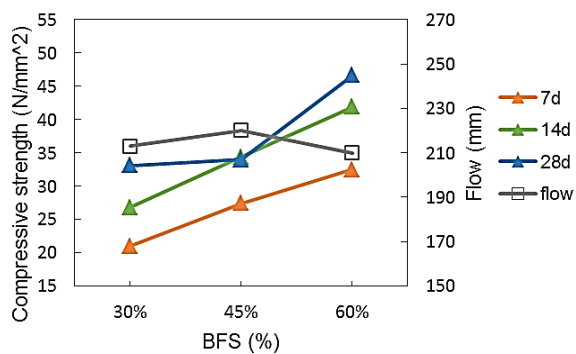

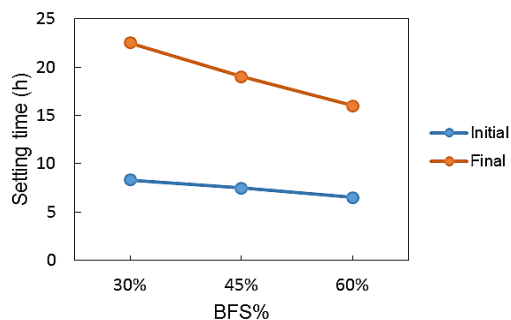Fig.5 Relationship between compressive strength, flow and BFS%

Fig.6 Relationship between BFS% and setting time

(4) Mixing time

As shown in Fig.7, at a low BFS% (30%), the compressive strength and flow values increased when mixing time is less than 390s. Beyond 390s, however, the compressive strength decreased slightly and the flow value changed little. It is possible to deduce that 390s could be mixing time for an optimal compressive strength and flow in case of slag content of 30%.

As shown in Fig.8, at a high BFS% (60%), changes of the strength and flow values were quite complicated with the change of mixing time. All the

data could be analyzed on 3 ranges (270s-330s, 330s-390s, 390s-450s). In the range of 270s-330s, both compressive strength and flow values increased. But decrease in the range of 330s-390s for 14d and 28d compressive strength and an increase in 7d compressive strength and flow. In the range of 390s-450s, the 28d compressive strength increases slightly while 7d and 14d compressive strength decrease gently. Meanwhile, the increasing trend of the flow changes from steep to gentle shape. In summary, a relatively high early compressive strength can be obtained by mixing time 390s. From the perspective of 28d compressive strength, the optimal mixing time could be controlled around 330s. The increasing trend of flow was similar to the trend for 30% BFS. An optimal flow value could be chosen when the mixing is also around 330s.
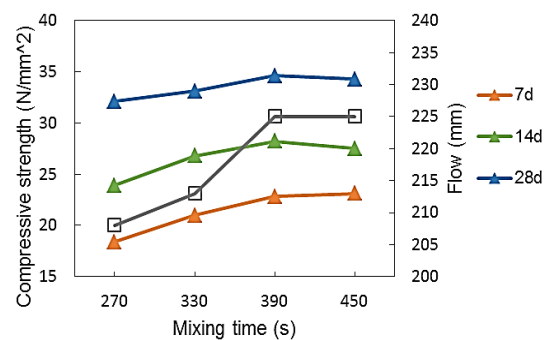

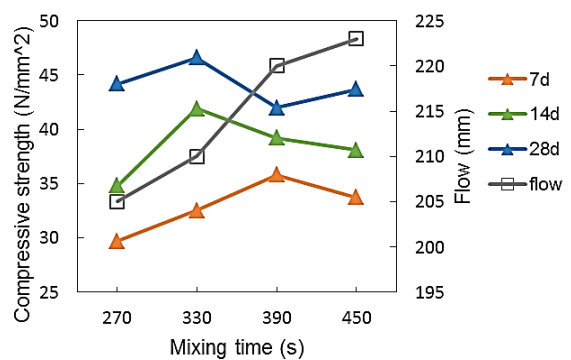Fig.7 Relationship between compressive strength, flow and mixing time at 30% BFS%

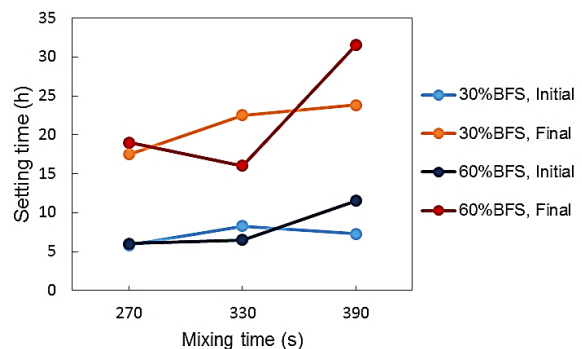Fig.8 Relationship between compressive strength, flow and mixing time at 60% BFS%

Fig.9 Relationship between mixing time and setting time

According to Fig.9, the trend of setting time for 30% BFS and 60% BFS were different. With the increase of mixing time, the trend of setting time was convex when the slag content was 30%. The initial setting changes little while the final setting time extended and more gently beyond 330s. On the contrary, when the slag content was 60%, the trend of setting time was concave. The initial setting time is extended more steeply as the mixing time beyond 330s. In the range of 270s-330s, the final setting time decreases but increases steeply in the range of 330s-390s.

Theoretically, the extension of mixing time would contribute to the dissolution of solid activator $Na_2SiO_3 \cdot 9H_2O$. When the mixing time is extended, the content of soluble silicate mass can be increased in the fresh mortar. At the same time, the water content increases as well. An increase of soluble silicate mass is good for generating the geopolymer gel quickly and completely. Thus, the compressive strength can be improved with the increase of mixing time. On the other hand, due to the release of crystallization water from $Na_2SiO_3 \cdot 9H_2O$, the flow value is increased and the setting time extended. Also, the growth of the released water may increase the porosity causing the loss of compressive strength. The apparent change of the flow, setting time and compressive strength with the change of mixing time appeared in the range of 330s-390s.

(5) Curing temperature

The relationship between curing temperature and compressive strength was shown in Fig.10. Unlike the conventional GP mortar, elevating the curing temperature prevented the development of the compressive strength and reduced the 28d compressive strength. It can be explained by two reasons.
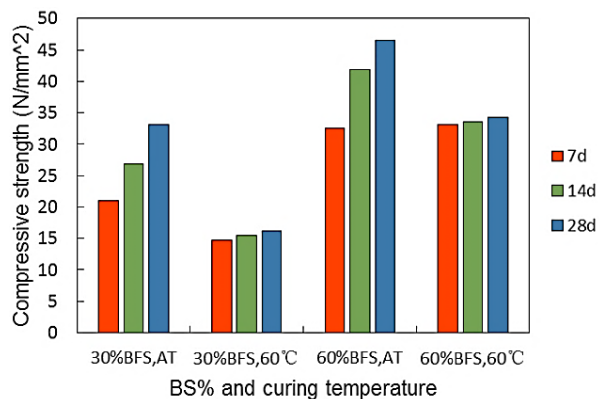

Fig.10 Relationship between curing condition and compressive strength

Since FA-based reaction is dominated in higher temperature, an elevated curing temperature would hinder the formation of C-A-S-H gel which is from BFS-based reaction. For FA/BFS based GP mortar, the compressive strength is obtained from normal geopolymer gel N-A-S-H and C-A-S-H gel. Namely, elevated curing temperature results in less reaction of BFS in binders, leading to lower compressive strength.

3. MICROSTRUCTURAL CHARACTERISATION

3.1 Results and analysis of XRD

XRD patterns of FA, BFS and hardened GP paste were shown in Fig.11. It could be found that the main phases formed in the BFS, FA and hardened GP paste are amorphous. Compared the traces of BFS with hardened GP paste (case 1 of 28d and case 10 of 28d), most crystals of in BFS were transformed into the amorphous phases. However, the main crystals in FA retained in the GP paste. A new peak which represents the calcite appears at the 29 ° 2 Theta degree. Since the content of calcium was low in FA, it could be considered that the appearance of calcite was related to some reaction occurred in BFS. It is still unclear and needs to be clarified in future research.
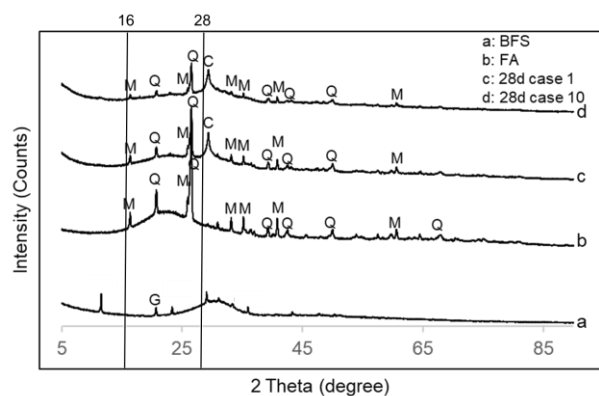

Fig.11 XRD of BFS, FA and hardened GP paste for 28d {G: Gehlenite; M: Mullite; Q: Quartz; C: Calcite}

A broad band with a relatively high intensity between 16°-28° indicated that FA had mixed semi-crystalline and amorphous structure, according to the XRD trace of FA. However, the XRD traces of case 1 (30%BFS) and case 10 (60%BFS) indicated smaller intensities between 16° and 28° which means that the GP paste had almost complete amorphous structure.

3.2 Results and analysis of SEM

Fig.12 and Fig.13 showed the SEM images of the cross-section of the hardened GP paste for case 1 and case 10 respectively. According to Fig.12, the hardened GP paste was heterogeneous and contained a large amount of unreacted fly ash. The gel formation of GP was incompact. Compared with case 1 (30% BFS), the micrographs of case 10 (60% BFS) presented an increasing homogeneity in the gel formation. In addition, the gel formation was more compact than that of case 1 with low slag content. This can explain why the compressive strength of the specimens with high slag content was higher than the specimens with low slag content.
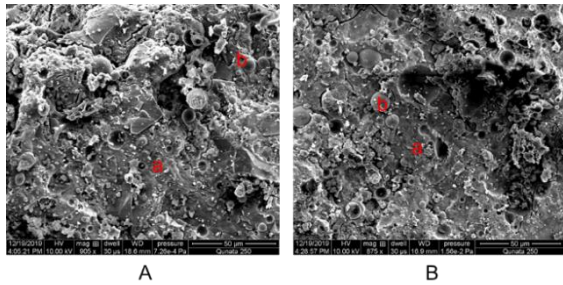
Fig.12 SEM images of the hardened GP paste for case 1. (a: Gel formation of GP; b: Unreacted sphere particles of FA)
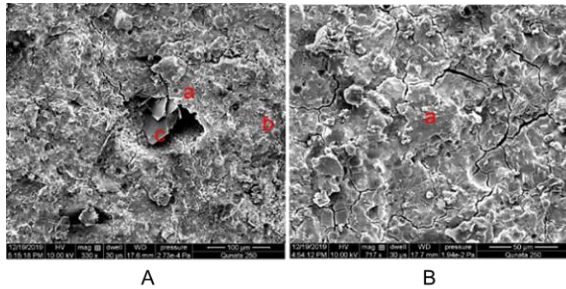

Fig.13 SEM images of the hardened GP paste for case 10. (a: Gel formation of GP; b: Unreacted sphere particles of FA; c: Crystalline of calcium hydroxide)

4. CONCLUSIONS

Flow, setting time and compressive strength of $Na_2SiO_3 \cdot 9H_2O$ activated geopolymer mortar was investigated in terms of the concentration of $Na_2SiO_3 \cdot 9H_2O$, mass ratio of alkaline activator to binder, slag content, mixing time and curing temperature. Results were shown as follows:

• An increase of SS% brought an improvement of compressive strength and a reduction of flow ability. Regarding the setting time, both initial and final setting time were shortened with an increase of SS%.

• With a rise of AA/AB, the compressive strength was decreased while the flow was increased. Regarding the setting time, it increased gentler after exceeding the value of 0.5, especially in the case of final setting time.

• Due to the existence of rich CaO in BFS, higher compressive strength and shorter setting time were obtained by an increase of BFS%. However, unlike the conventional geopolymer, it brought little influence on the flow values.

• The extension of mixing time in the range of 330-390s contributed to an improvement of compressive strength and an increase of flow significantly in the case of 30% of slag content. However, in the case of 60%, it only promoted the early compressive strength and flow as well. Regarding the setting time, longer mixing time mostly increases the initial and final setting time to various degrees.

• Elevated curing temperature led to lower compressive strength in comparison with those cured under ambient temperature due to a rich content of BFS.

• Based on the results of XRD and SEM, the reaction product of GP paste activated by $Na_2SiO_3 \cdot 9H_2O$ was almost with amorphous phase, similar to the conventional GP.

Above all, FA/BFS based geopolymer material activated by $Na_2SiO_3 \cdot 9H_2O$ can be synthesized with acceptable compressive strength and workability by well-designed proportions.

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