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Original Article

Characteristics of hybrid alkaline cement composites with high cement content: flash set and high compressive strength

Sungwoo Park, Kebede Alemayehu Moges, Siyu Wu, Sukhoon Pyo[*]

Department of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulju-gun, Ulsan, Republic of Korea

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ABSTRACT

This paper explores hybrid alkaline cement composites with high cement content over 50%. Calcium (Ca) accelerates the strength development and improves the compressive strength of geopolymer. However, the mixing proportion of Ca in geopolymer has been limited because Ca significantly decreases the flow of fresh geopolymer. This study resolves the flow decline issue by mixing a part of the initial mixing water with cement before adding it into a metakaolin-based geopolymer, which is named hybrid alkaline cement composites (HACC) in this study. The cement/(metakaolin + cement) ratio investigated is up to 85%. Based on the initial setting time and compressive strength results, some unique characteristics of the HACC are observed: i) the material is set within 10 min and the 28-day compressive strength is over 80 MPa with 1:1 mixing ratio of geopolymer and cement paste, and ii) the compressive strength of HACC is not always higher with a lower w/c ratio of cement paste.

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1. Introduction

This study was conducted based on the two questions: i) what is the effect of ordinary Portland cement (OPC) on geopolymer?, and ii) what is the effect of geopolymer on cement paste? With regard to the first question, geopolymer is a dominant matrix, and OPC is considered as an additive. Hence, this mixture possibly inherits most of the geopolymer characteristics, and OPC may participate in a part of a chemical reaction, although the influence of OPC on geopolymer reaction can be remarkable in some aspects. With regard to the second question, the cement paste is a dominant matrix, and geopolymer is an additive that has barely been studied. In either case, the main material occupies most of the matrix, whereas the secondary material takes a smaller portion. These two questions guided the authors to the boundary of the two cases, and a new question was derived: What characteristics would the material have if mixed with geopolymer and cement paste at a ratio of 1:1?

The main chemical component of OPC is calcium (Ca), and it has a considerable influence on the non-Ca geopolymer with a precursor that does not include Ca. The initial setting time of non-Ca geopolymer is usually 12–24 h or higher [1–6].

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[*] Corresponding author.
E-mail address: shpyo@unist.ac.kr (S. Pyo).

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This slow strength development can be a critical issue in terms of application despite the inherent advantages of non-Ca geopolymer that can utilize various industrial by-products and can reduce CO_2 emissions compared with OPC [7–12]. When Ca is added into a non-Ca geopolymer, it reduces the setting time remarkably, triggering the formation of calcium aluminosilicate hydrate (C-A-S-H) gels. Ground-granulated blast-furnace slag (GGBS) has been reported to decrease the initial setting time of geopolymer to 40–50 min with 30%–40% replacement [3,4], and OPC to 40 min with 12% replacement [2]. Furthermore, GGBS and OPC can improve the compressive strength of non-Ca geopolymers.

Although Ca has beneficial effects on geopolymer, the dosage is limited; the replacement ratio of the precursor of non-Ca geopolymer with GGBS was reported to be approximately 40%–50% [3,4,13,14], and the ratio with OPC was approximately 12%–15% [2,15]. The maximum compressive strength can be achieved with the maximum dosage of the Ca sources, which raises the question on the compressive strength with a higher dosage. The main reason for the limitation of the dosage of Ca sources is assumed to be due to Ca sources decreasing the workability of geopolymer severely [2,4,15].

If Ca in OPC is the one that decreases the setting time and increases the compressive strength of geopolymer, as insisted by the previous studies, it can be hypothesized that the setting time and compressive strength of geopolymer can be further improved with a higher OPC content beyond previously known limits. To break the limit of OPC content caused by the low workability, this study proposes the addition of cement paste into geopolymer instead of OPC; cement paste is a mixture of OPC and water. The proposed mixing method remarkably improved the workability of the fresh mixture and enables the exploration of the mysterious geopolymer material with a replacement ratio with OPC of more than 50% [6].

This study aims to introduce the properties of the mixture of a geopolymer and cement paste with various mixing proportions, mainly focusing on the compressive strength and initial setting time. It is hypothesized that an optimum proportion of cement paste in the mixture results in the highest compressive strength, and the optimum proportion can be dependent on other design variables. Metakaolin was used as a precursor because its quality is consistent. Various mix designs were applied to investigate the factors contributing to the compressive strength and initial setting time. The effect of cement paste on these properties and the effect of geopolymer on cement paste are also discussed. Thermogravimetric analysis (TGA) and scanning electron microscope (SEM) with energy dispersive microscope (EDS) were conducted to inspect the change of the chemical structure of the mixture with the mixing proportion and the water to cement (w/c) ratio of cement paste and the silicon to aluminum molar (S/A) ratio of geopolymer.

Lastly, this paper refers to the mixture of geopolymer and cement paste “hybrid alkaline cement composite” (HACC), as a synergistic effect on the compressive strength was observed. Although a similar application of OPC into geopolymer can be found in previous studies of hybrid alkaline cement (HAC), HACC has a different mix design concept. The development of HAC aims to achieve environmental benefits by reducing OPC content in a binder. A typical OPC content in HAC is limited to 30% [16–23], and a small amount of alkaline activated solution results in a shorter setting time compared with cement paste. However, the mix design variables of HACC directly come from those of geopolymer and cement paste, and HACC does not have a limitation on the content of OPC and alkali solution. The HACC can be characterized by good workability, fast setting, and high 28-day compressive strength, which is distinctive from HAC because the usual compressive strength of HAC is lower than or similar to that of cement paste [20,24].

2. Materials and methods

2.1. Raw material and mix design

Commercial products of metakaolin, OPC type I, and silica fume were used, and their chemical compositions are shown in Table 1. A geopolymer was synthesized using a metakaolin and a sodium silicate solution. The sodium silicate solution was prepared by dissolving silica fume in sodium hydroxide solution. The solution was sealed and placed in an oven at 75 °C for more than 12 h to extend the dissolution rate of silica fume [25,26]. Silica fume was used to adjust the total S/A ratio of the geopolymer. The geopolymer was synthesized to have three different S/A ratios of 1.0, 1.4, and 1.8. The modulus of the alkali activator increased with an increase in the S/A ratio from 1.4 to 1.8. From preliminary tests, the compressive strength of the geopolymer was highest at the S/A 1.8, and severely decreased thereafter [27,28]. Notably, the silicon in OPC was not involved in the S/A ratio. The geopolymer with an S/A ratio of 1.0 was synthesized using sodium hydroxide solution, not sodium silicate solution. The sodium to aluminum molar (N/A) ratio was 1.0 for all specimens, except for the specimen with an S/A ratio of 1.0; at an S/A ratio of 1.0, the alkalinity of the solution with an N/A ratio of 1.0 was so high that it retards the initial setting time; therefore, an N/A ratio of 0.8 was used to achieve an alkalinity similar to that of the solution with an S/A ratio of 1.4. The water-to-solid (w/s) ratio was 0.45 for all geopolymer specimens. A summary of geopolymer mixing proportions are shown in Table 2. The w/c ratios of cement paste mixed with the geopolymers were from 0.36 to 0.48. Preliminary tests confirmed that w/c ratios above 0.48 resulted in a lower compressive strength, which can be attributed to the excessive amount of water, and these data were excluded in this study. The mixing proportions of the cement paste in the HACC were 0%, 25%, 50%, 75%, and 100%

Table 1 – Chemical compositions of the raw materials used in this study (%).

Constituent	Metakaolin	OPC	Silica fume
SiO_2	50.37	19.38	97.30
Al_2O_3	43.33	4.48	0.06
CaO	0.45	64.48	0.09
Fe_2O_3	2.82	3.46	0.19
TiO_2	2.29	0.29	0.00
MgO	0.15	2.82	0.42
SO_3	0.05	3.31	0.90

Table 2 – Mix designs of the HACC (g/kg).

Specimen design			Geopolymer				Cement paste	
S/A	w/c	Mix[a]	MK[b]	SF[c]	NaOH	Water	Cement	Water
1.8	0.36	0%	338.63	169.05	131.98	310.34	–	–
		25%	291.47	126.79	98.99	232.76	183.82	66.18
		50%	194.31	84.52	65.99	155.17	367.65	132.35
		75%	97.16	42.26	33.00	77.59	551.47	198.53
		100%	–	–	–	–	735.29	264.71
1.8	0.42	25%	291.47	126.79	98.99	232.76	176.06	73.94
		50%	194.31	84.52	65.99	155.17	352.11	147.89
		75%	97.16	42.26	33.00	77.59	528.17	221.83
		100%	–	–	–	–	704.23	295.77
1.8	0.48	25%	291.47	126.79	98.99	232.76	168.92	81.08
		50%	194.31	84.52	65.99	155.17	337.84	162.16
		75%	97.16	42.26	33.00	77.59	506.76	243.24
		100%	–	–	–	–	675.68	324.32
1.4	0.48	0%	442.06	97.47	150.13	310.34	–	–
		25%	331.54	73.11	112.59	232.76	168.92	81.08
		50%	221.03	48.74	75.06	155.17	337.84	162.16
		75%	110.51	24.37	37.53	77.59	506.76	243.24
1.0	0.48	0%	542.31	–	147.34	310.34	–	–
		25%	406.73	–	110.50	232.76	168.92	81.08
		50%	271.16	–	76.67	155.17	337.84	162.16
		75%	135.58	–	36.83	77.59	506.76	243.24

[a] Mixing proportion of cement paste.

[b] Metakaolin.

[c] Silica fume.

by weight; 0% and 100% indicate geopolymer and cement paste alone, respectively.

The HACC specimens were prepared through the following procedure: i) metakaolin and sodium silicate solution were mixed for 5 min, and the mixing bowl was sealed to prevent drying, ii) OPC and water were mixed for 5 min, iii) the cement paste was poured into the geopolymer and mixed for 1 min at a high speed because of the fast setting, and iv) the mixture was cast in molds, vibrated for 2 min to remove air bubbles, and sealed. The specimen preparation procedure is also summarized in Fig. 1. With this method, the flow level of the mixture increases considerably compared with the powder mixing of metakaolin and OPC. Notably, in the case of the 50% mixing proportion, the flow level was greater than 250 mm, whereas the powder mixing was not applicable because the mixture was too stiff. After one day, the specimens were taken out of the molds and kept in plastic bags sealed at a room temperature until tested.

2.2. Initial setting time

The initial setting time was investigated following ISO 9597:2008 [29]. In the case of the HACC, the elapsed time was calculated after the geopolymer and cement paste were mixed. In the cases of geopolymer and cement paste, the elapsed time was calculated after the initial contact of solution and metakaolin or water and OPC.

2.3. Compressive strength

The specimens were cast in $50 \times 50 \times 50$ mm^3 cubic molds. The compressive strength test was conducted in accordance with ASTM C39 [30]. Three replicates were tested, and the average value was used for the representative compressive strength at 7 and 28 days.

2.4. TGA and SEM

TGA (Q500, TA Instruments) and SEM (Nova NanoSEM, FEI) tests were performed. Specimens were cast in vials. The specimen was 10×40 mm^2 in size and cylindrical. After curing, the specimens were ground using a mortar and pestle for TGA tests and broken into small pieces for SEM tests. The ground or broken specimen was submerged in isopropanol (10 mL/g) for 1 h to replace the free water with isopropanol [31]. After filtering the suspension, the specimens were dried in a vacuum, further dried in an oven at 40 °C for 10 min, and kept in a desiccator until tested. TGA tests were performed at a rate of 10 °C/min starting from 30 °C up to 900 °C.

3. Results and discussions

3.1. Compressive strength

3.1.1. Effect of the w/c ratio of cement paste

The 7- and 28-day compressive strength results of the HACC with cement pastes of different w/c ratios are shown in Fig. 2. The x-axis is the mixing proportion of the cement paste by weight, and the y-axis is the compressive strength. The total water content is also included in the figure, as it is an important variable. The mixing proportions of 0% and 100% in the x-axis indicate geopolymer and cement paste alone, respectively. The S/A ratio of the geopolymer was 1.8 and it

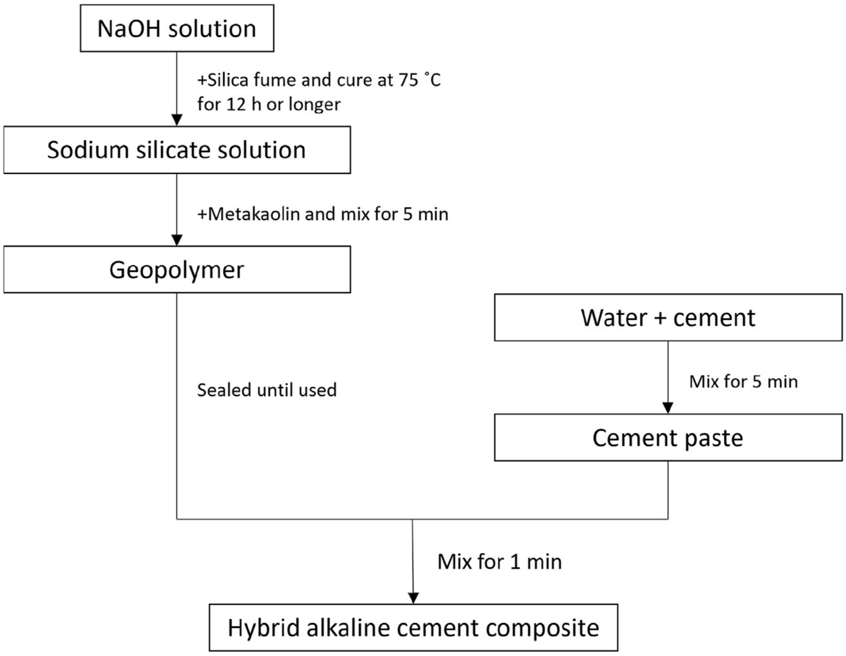
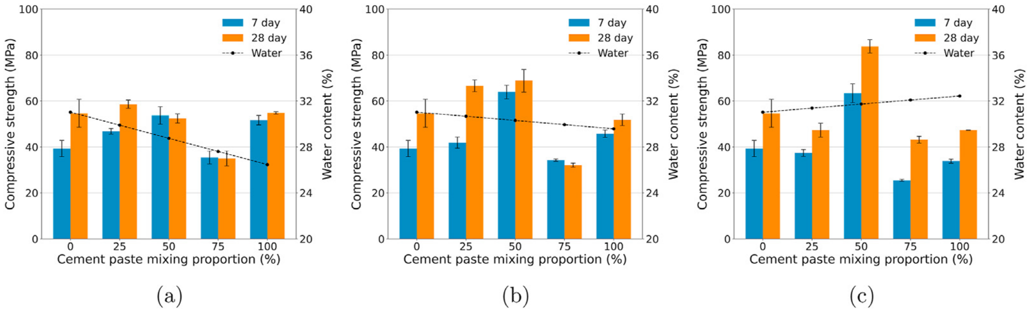


Fig. 1 – HACC specimen preparation procedure.



(a) (b) (c)

Fig. 2 – Compressive strength of the HACC with geopolymer at an S/A ratio of 1.8 and cement paste at w/c ratios of: (a) 0.36, (b) 0.42, and (c) 0.48.

was mixed with the cement paste with w/c ratios of 0.36, 0.42, and 0.48.

The effect of the mixing proportion of cement paste on the compressive strength of the HACC is substantial. The 25% HACC data show the effect of cement paste on the compressive strength of the geopolymer as geopolymer is the dominant structure. Cement paste enhances the compressive strength of the geopolymer; the compressive strength of the 25% HACC is higher than that of 0% HACC, which is identical to the previous studies [2]. The cement paste with a w/c ratio 0.48 degrades the compressive strength of the geopolymer, which is assumed to be because of the excessive water in cement paste, creating pores inside. The 75% HACC data show the effect of the geopolymer on the compressive strength of cement paste, as cement paste is the dominant structure. The geopolymer adversely affects the compressive strength of cement paste; the compressive strength of the 75% HACC is lower than those of cement paste. Sodium hydroxide decreases the compressive strength of cement paste [32–34] by increasing the capillary porosity [32,34,35] and by reducing the density of calcium silicate hydrate (C–S–H) [32,35,36]. Given that sodium hydroxide solution is a basic ingredient of geopolymer, it can probably degrade the main matrix of cement paste in the mixture in the similar way. As a result, the 75% HACC generally exhibits the lowest compressive strength in this study.

The synergistic effect of geopolymer and cement paste can be observed in the 50% HACC, as its compressive strength is higher than those of geopolymer and cement paste. The 50% HACC with cement paste with a w/c ratio of 0.48 results in compressive strengths of 63 MPa at 7 days and 84 MPa at 28 days. Given that the w/s ratio of the HACC is 0.46, the compressive strength value is remarkably high compared with that of cement paste. In summary, the compressive strength of the HACC is highly dependent on the mixing proportion of cement paste.

Notably, the cement paste with a w/c ratio of 0.36 does not have a synergistic effect on the compressive strength with the 50% HACC; the compressive strength of the 50% HACC is similar to that of cement paste and is lower than that of the

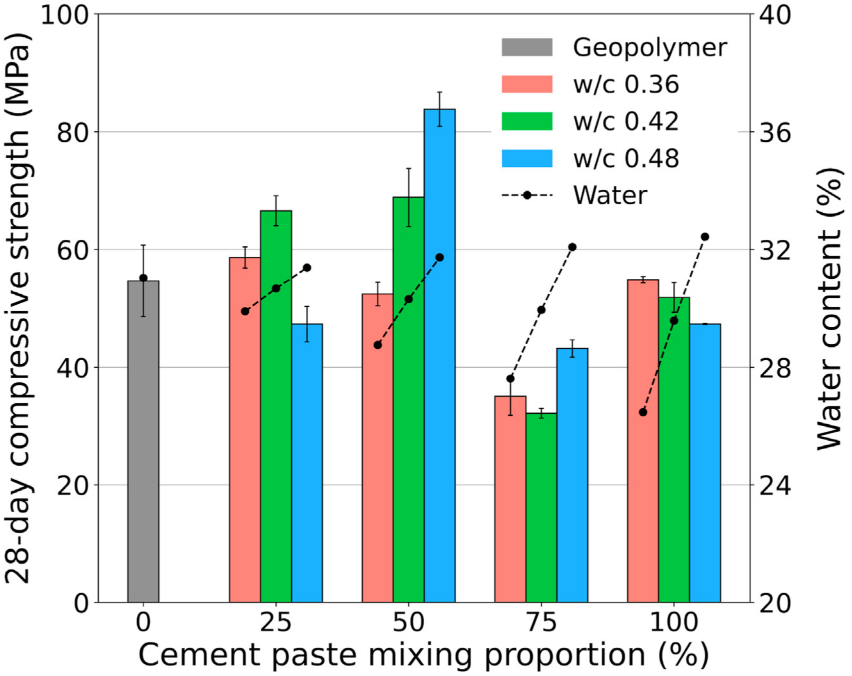
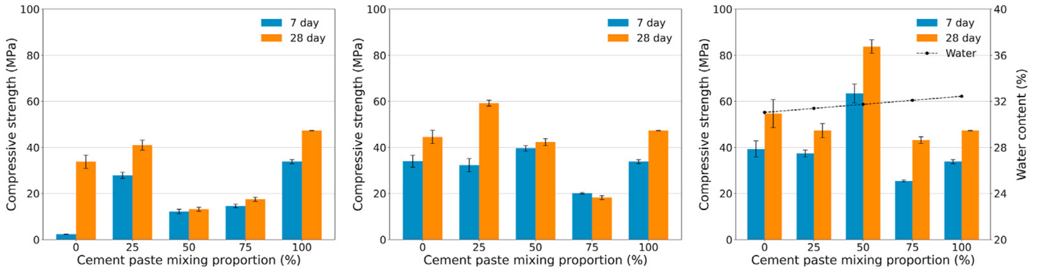


Fig. 3 – 28-day compressive strength of the HACC with the geopolymer with an S/A ratio of 1.8 and the cement paste with w/c ratios of 0.36, 0.42, and 0.48.

25% HACC at 28 days. The amount of water in the cement paste with a w/c of 0.36 is smaller than those with w/c ratios of 0.42 and 0.48. A lower amount of mixing water does not always yield a higher compressive strength of HACC, which is peculiar characteristics of HACC. Hence, the amount of water is important for a high compressive strength.

Another clue of the importance of water in the mixture of geopolymer and cement paste can be found in Fig. 2. At a w/c ratio of 0.36, the compressive strength is increased from 7 days to 28 days only in the 25% mixing proportion. At a w/c ratio of 0.42, the compressive strength is significantly increased in the 25%, slightly in the 50%, and barely in the 75% mixing proportion. At a w/c ratio of 0.48, the compressive strength increases in all of the mixing proportions from 25% to 75%. This indicates that an adequate amount of water is required for the strength development of the HACC because of the existence of the Ca phases. When Ca is added into non-calcium aluminosilicate geopolymer, it changes the geopolymer structure, adding C–S–H, C-A-S-H gels, and CAH gels, which exhibit hydration [37–42]. Therefore, an HACC with a higher amount of cement paste can have a higher degree of hydration requiring a larger amount of the initial mixing water.

Fig. 3 shows the 28-day compressive strength data of the HACC extracted from the data in Fig. 2. The use of cement paste with a higher w/c ratio results in a higher compressive strength as the mixing proportion increases. The highest compressive strengths of the 25% and 50% HACCs are achieved by the cement pastes with w/c ratios of 0.42 and 0.48, respectively. This trend is extraordinary compared with cement paste or geopolymer alone. Although cement paste needs water for hydration, the cement paste of a lower w/c ratio generally yields a higher compressive strength. The main role of water in geopolymer is just medium; whether geopolymer is hydrated or not is arguable between researchers; the amount of water chemically or physically bound is only approximately 6% [43,44]. Most of the initial mixing water does not play an important role for the strength development



(a) (b) (c)

Fig. 4 – Compressive strength of the HACC with cement paste with a w/c ratio of 0.48 and geopolymer with S/A ratios of: (a) 1.0, (b) 1.4, and (c) 1.8.

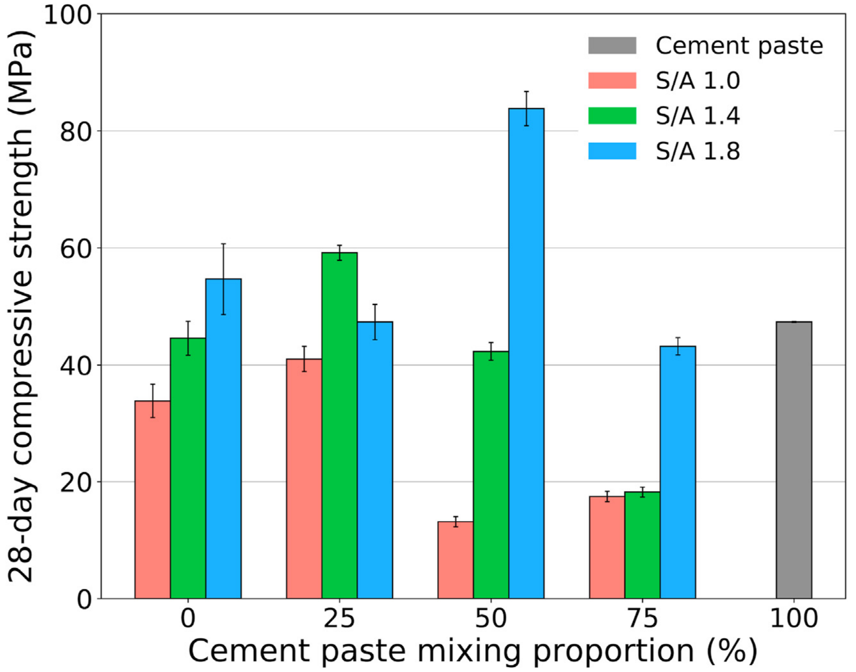


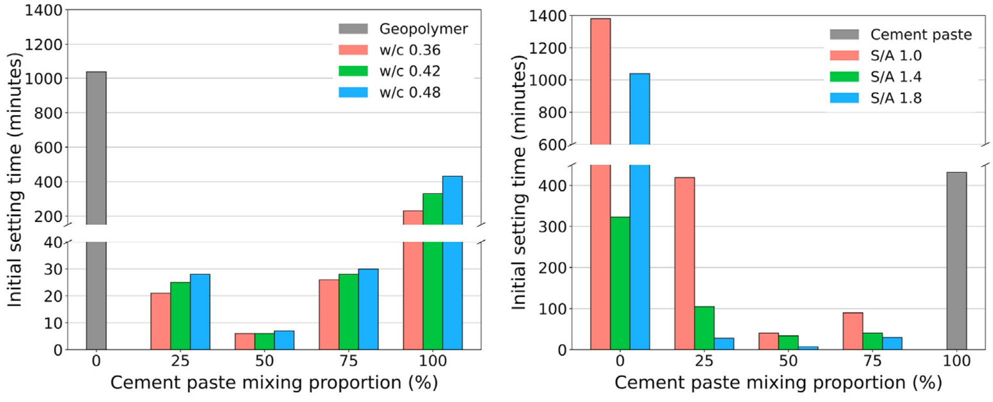
Fig. 5 – 28-day compressive strength of the HACC with the cement paste with a w/c ratio of 0.48 and the geopolymer with S/A ratios of 1.0, 1.4, and 1.8.

of geopolymers, creating macro-sized pores in the system [44] and, thus, showing a linear decrease with the increase of the initial mixing water [45]. However, HACC does not follow the typical trend of a decrease in the compressive strength of the material as water content is increased.

3.1.2. *Effect of the S/A ratio of geopolymer*

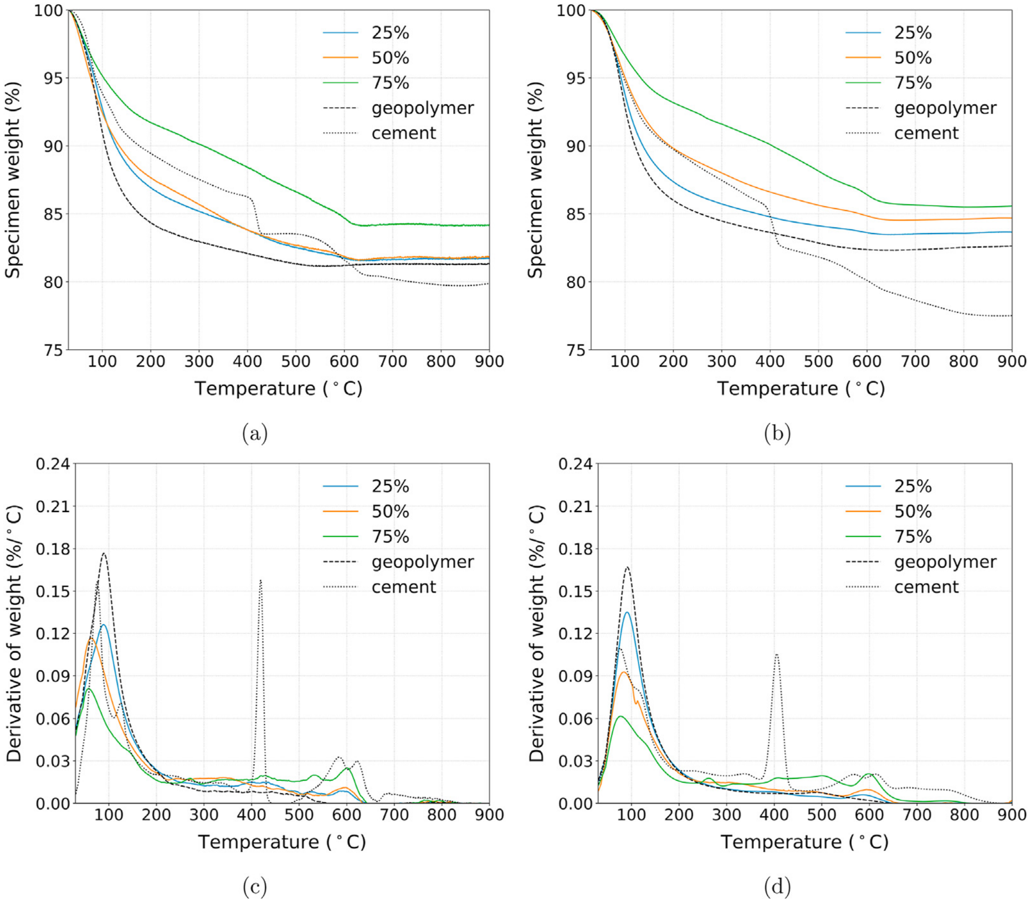
The 7- and 28-day compressive strength results of the HACC with the geopolymer of different S/A ratios are shown in Fig. 4. The S/A ratio of the geopolymer affects the development of the compressive strength of the HACC. In the specimen with an S/A ratio of 1.0, as the mixing proportion of cement paste increases, the strength development from 7 days to 28 days decreases. The largest increase is shown in the 0% mixing proportion (geopolymer), a small increase is found in 25%, and no increase is observed thereafter. The compressive strength of the HACC with an S/A of 1.4 increases up to 25% mixing proportion, and the HACC with an S/A 1.8 exhibits compressive strength development in all of the mixing proportions. It is noted that a higher S/A ratio indicates a larger content of sodium silicate in geopolymer, and the specimen with an S/A of 1.0 was synthesized using sodium hydroxide solution. Therefore, Sodium silicate plays an important role in the compressive strength development of HACC.

Fig. 5 shows the 28-day compressive strength data from the data in Fig. 4. The compressive strength of HACC is higher with a higher S/A ratio when the mixing proportion of cement paste is higher; the 25% and 50% HACC specimens have the highest compressive strengths with the geopolymer with S/A ratios of 1.4 and 1.8, respectively. Furthermore, the effect of



(a) (b)

Fig. 6 – Initial setting time of the HACC: (a) geopolymer with an S/A ratio of 1.8 and cement pastes with w/c ratios of 0.36, 0.42, and 0.48; and (b) cement paste with a w/c ratio of 0.48 and geopolymer with S/A ratios of 1.0, 1.4, and 1.8.



(a) (b)

(c) (d)

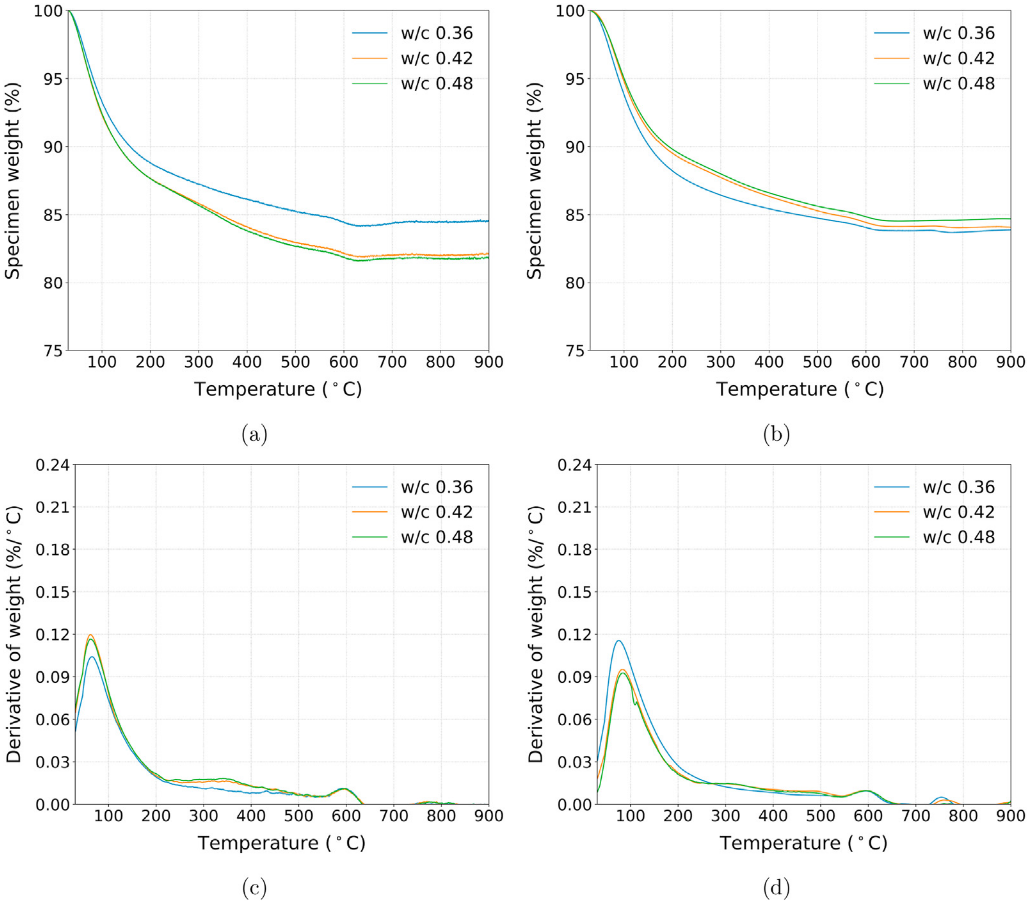
Fig. 7 – Effect of mixing proportion of cement paste on the TGA results. The HACC synthesized with an S/A ratio of 1.8 geopolymer and a w/c ratio of 0.48 cement paste: specimens at 7 days ((a) and (c)); and at 28 days ((b) and (d)).

the S/A ratio on the compressive strength is more substantial when the mixing proportion of cement paste is higher; the differences of the compressive strength among the HACC specimens with different S/A ratios becomes larger in the case of the 50% HACC than the 25% HACC. These results support that sodium silicate plays a critical role in strength development of HACC. As the S/A ratio increases, the formation of N-A-S-H gel network increases [46], and the N-A-S-H gel can uptake Ca, creating an (N,C)-A-S-H structure [47], which is closely related to the compressive strength of a material [48].

3.2. *Initial setting time*

The initial setting time test results of HACC specimens are shown in Fig. 6; Fig. 6a and b shows the effects of the w/c ratio of cement paste and the S/A ratio of geopolymer, respectively. For both cases, the mixing proportion of cement paste substantially affects the initial setting time of HACC. At up to 50% mixing proportion, the initial setting time of HACC decreases; especially, some of the 50% HACC specimens set within 10 min. This result is in accordance with the previous observation that Ca phases accelerate the initial setting of non-Ca geopolymer [2]. It should be noted that the conventional method of the initial setting time measurement used in this study is not suitable to see the deliberate differences among the 50% HACC specimens because the material sets too fast during a vicat test; therefore, a proper method needs to be developed. The results of the 75% HACC specimens prove that geopolymer can decrease the initial setting time of cement paste. The 75% HACCs set slower than the 50% HACCs, even though 75% HACCs have higher Ca contents. Therefore, the Ca-to-geopolymer ratio may be an important factor in the initial setting time of HACC. As a result, the mixing proportion of cement paste is also a dominant factor in the initial setting time of HACC.

In Fig. 6a, the w/c ratio of cement paste is also involved in the initial setting time of HACC. All of the specimens with cement paste of a lower w/c ratio set faster, which is assumed to be because of the higher concentration of Ca in the HACC. Fig. 6b shows a clear correlation between the S/A ratio of geopolymer and the initial setting time of HACC; a higher S/A ratio results in a faster initial setting time of the HACC when the cement mixing proportion is the same. The effectiveness of the S/A ratio of geopolymer is more significant than the w/c ratio of cement paste. The geopolymer specimen with a higher S/A ratio contains a higher amount of sodium silicate, which is known to accelerate cement hydration [49]. Therefore, the two different acceleration mechanisms are assumed to be combined in the chemical reaction of HACC; the combination of geopolymer and cement paste possibly decreases their



(a) (b)

(c) (d)

Fig. 8 – TGA results of the 50% HACC synthesized with an S/A ratio of 1.8 geopolymer and the cement pastes with different w/c ratios: specimens at 7 days ((a) and (c)) and at 28 days ((b) and (d)).

initial setting times by the Ca in cement paste, reacting with geopolymer and the sodium silicate in geopolymer, accelerating cement hydration.

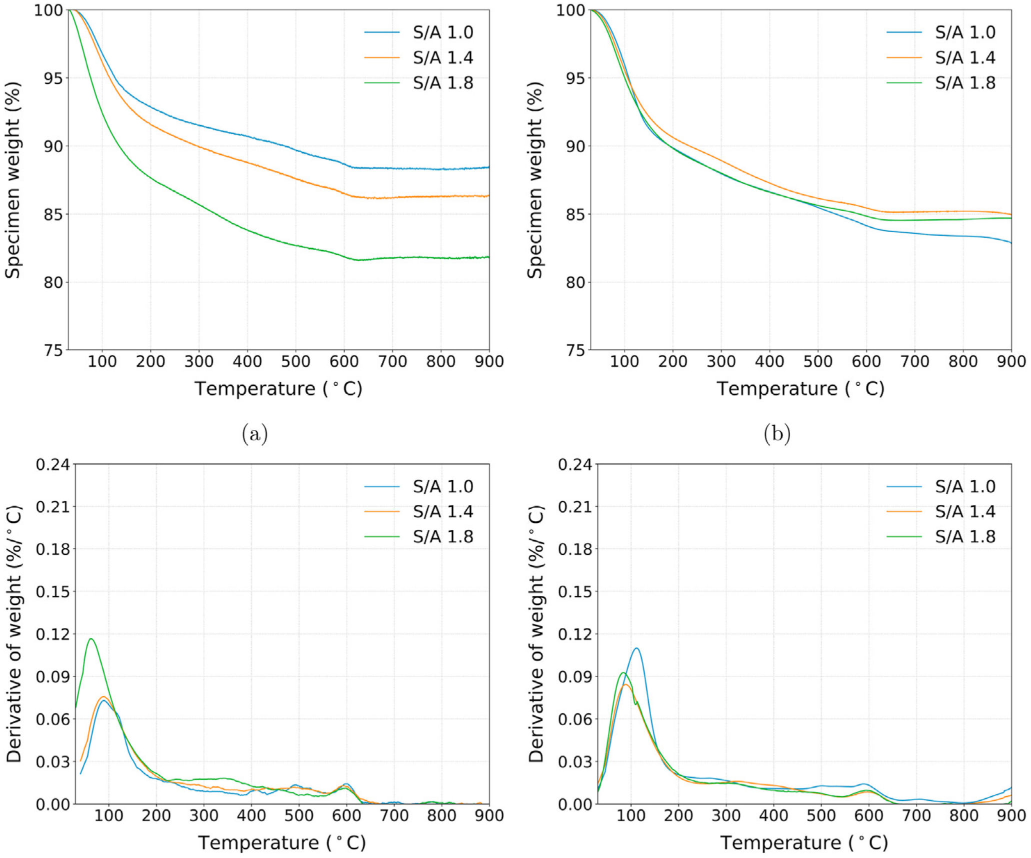
3.3. TGA

The TGA results of the HACCs with different mixing proportions of cement paste are shown in Fig. 7. The S/A 1.8 geopolymer and the w/c 0.48 cement paste were mixed. Fig. 7a and b correspond to the weight loss data, and Fig. 7c and d correspond to the derivative of the weight loss data. The left (Fig. 7a and c) and right (Fig. 7b and d) columns show the results of the specimens cured for 7 and 28 days, respectively.

Curing age affects the TGA data of all of the specimens. The total mass loss up to 900 °C of geopolymer and HACC decreases from 7 day-curing to 28 day-curing, whereas that of cement paste increases. Water is chemically bound to the hydrated cement paste; thus, the weight loss is greater at 28 days than at 7 days. However, the geopolymer shows an opposite trend; the gradual mass loss in TGA decreases as the curing age of geopolymer increases. The weight loss of geopolymer up to 300 °C is associated with the water chemically bound [50], and above 300 °C with the dehydroxylation of OH groups in a geopolymer structure [51]. As the geopolymer reaction continues, the condensation process produces additional water from OH groups [44], and the additional water is already removed during the sample preparation. Therefore, the amount of dehydroxylation of OH groups in geopolymer decreases with an increase of curing time, which results in a smaller weight loss in TGA. Based on this viewpoint, it can be concluded that the strength development of HACC after 7 days is mainly caused by the growth of the geopolymer structure.

The weight of HACC decreases more slowly above 100 °C as the mixing proportion of cement paste increases. This means that the amount of N-A-S-H gels in HACC decreases with a higher mixing proportion because the geopolymer exhibits more significant weight loss up to 200 °C compared with cement paste. Especially, the 50% HACC at 28 days follows the line of cement paste up to 200 °C, which implies that the weight loss from N-A-S-H gels in the 50% HACC is minimal.

The 75% HACC yields a peculiar curve in TGA data, meaning that its chemical structures are different from those of cement paste and the geopolymer. The weight loss of the 75% HACC at 40–150 °C can be associated with the cement paste because its derivative curve is similar to that of the cement paste; the curves have the first peak at approximately 90 °C and the second peak at around 110 °C, which are associated with the decomposition of ettringite and C–S–H. However, the amount of these hydrate phases in the 75% HACC seems less than that of cement paste based on the less weight loss up to 150 °C. The gradual weight loss after 200 °C indicates the structures of the 75% HACC are different from



(a) (b) (c) (d)

Fig. 9 – TGA results of the 50% HACC synthesized with a w/c ratio of 0.48 cement paste and the geopolymer with different S/A ratios: specimens at 7 days ((a) and (c)) and at 28 days ((b) and (d)).

those of other specimens. Further studies, such as thermodynamic analysis accompanied with x-ray diffraction, are required to reveal the chemical components. In conclusion, the addition of cement paste into a geopolymer creates more hydrated phases, although the phases can be different with a different mixing proportion.

HACC does not have portlandite. In derivative plots in Fig. 7c and d, only the cement paste shows a peak at 400 °C at which portlandite is decomposed. However, it is not shown in all of the HACCs. Previous studies suggest that portlandite is transformed to another hydrated phases, enhancing the compressive strength of HACC by filling voids [17,20,52]. Therefore, the transformation of the portlandite in the HACC can be a clue of its compressive strength that is even higher than those of geopolymer and cement paste.

Fig. 8 shows the TGA results of the 50% HACC with different w/c ratios of cement paste. The decrease of the weight loss up to 900 °C from 7 days to 28 days is related to the strength development of HACC. The total weight loss of the HACCs synthesized with the cement pastes with w/c ratios of 0.42 and 0.48 decreases, whereas that of the HACC with a w/c ratio of 0.36 does not. The compressive strengths of the HACCs with w/c ratios of 0.42 and 0.48 are improved from 7 days to 28 days, whereas that of the HACC with a w/c ratio of 0.36 does not. This result implies that the strength development of HACC from 7 days to 28 days is highly related to the condensation process in a chemical reaction of geopolymer that produces additional water [44]. Furthermore, the results indicate that the 50% HACC mixed with the cement paste with a w/c ratio of 0.36 or lower does not exhibit the growth of N-A-S-H gels.

Different trends of TGA results are observed between 7 and 28 days in Fig. 8. An HACC with a lower w/c ratio exhibits less total weight loss at 7 days, which is opposite to the trend observed at 28 days. Given that the effect of N-A-S-H gels on the TGA result is more significant at 7 days, it is assumed that a higher content of Ca in the HACC with a lower w/c ratio results in a less amount of N-A-S-H gels [22]. However, it was found that the weight loss from N-A-S-H gels becomes negligible by comparing the TGA results of the 50% HACC and the cement paste in Fig. 7. Therefore, a higher total weight loss of the HACC with a lower w/c at 28 days can be associated with a higher amount of hydrated products due to a higher content of Ca.

Fig. 9 shows the TGA results of the 50% HACCs with different S/A ratios of geopolymer. When the weight loss of a specimen up to 900 °C decreases, its compressive strength increases from 7 days to 28 days. Each specimen yields a distinct curve at 7 days, however, the curves become less distinct at 28 days. The weight loss of the HACC with the S/A 1.8 geopolymer decreases from 7 days to 28 days, which is assumed to be because of the condensation of OH groups in the chemical structures. It should be noted that only the

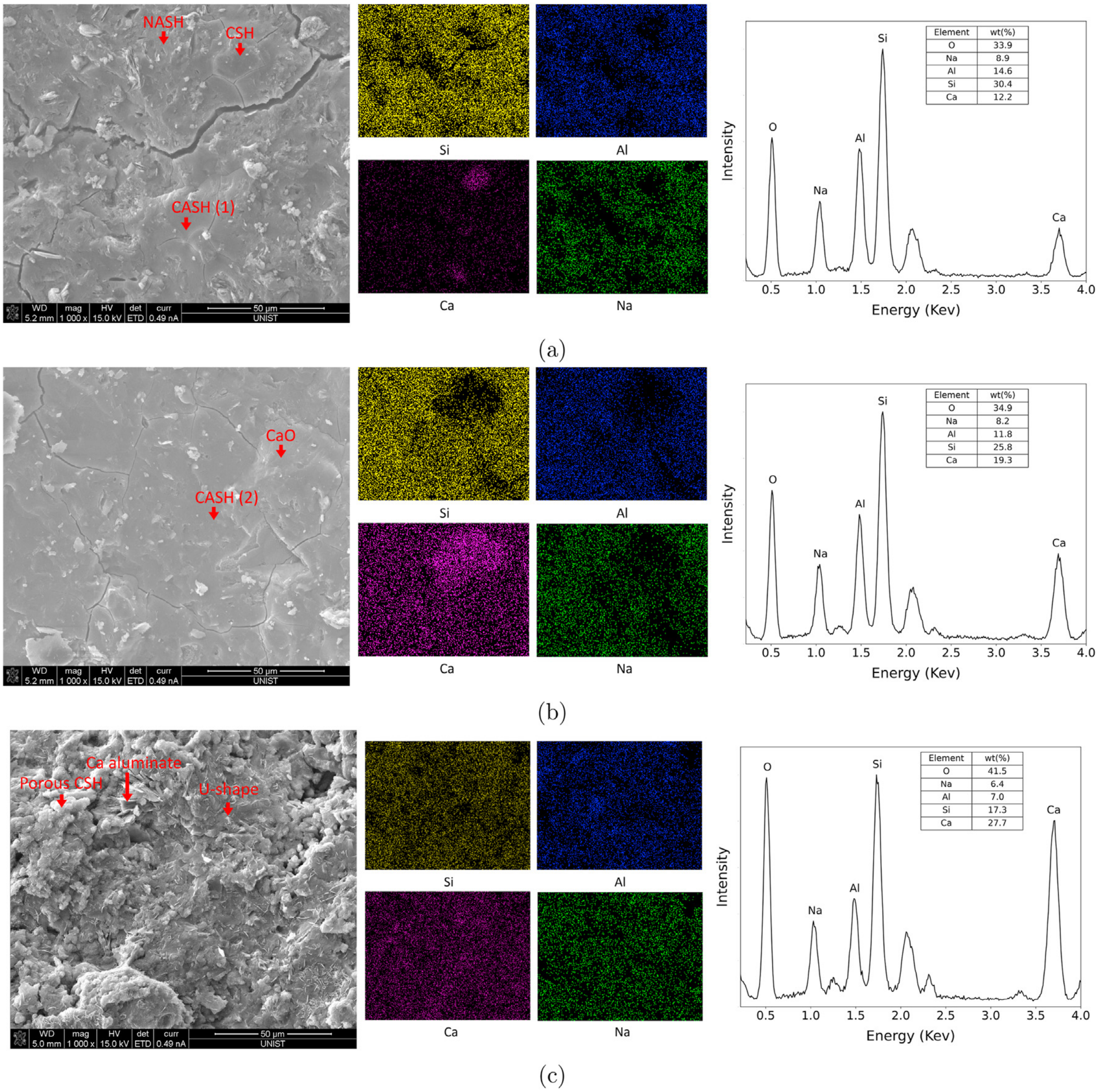
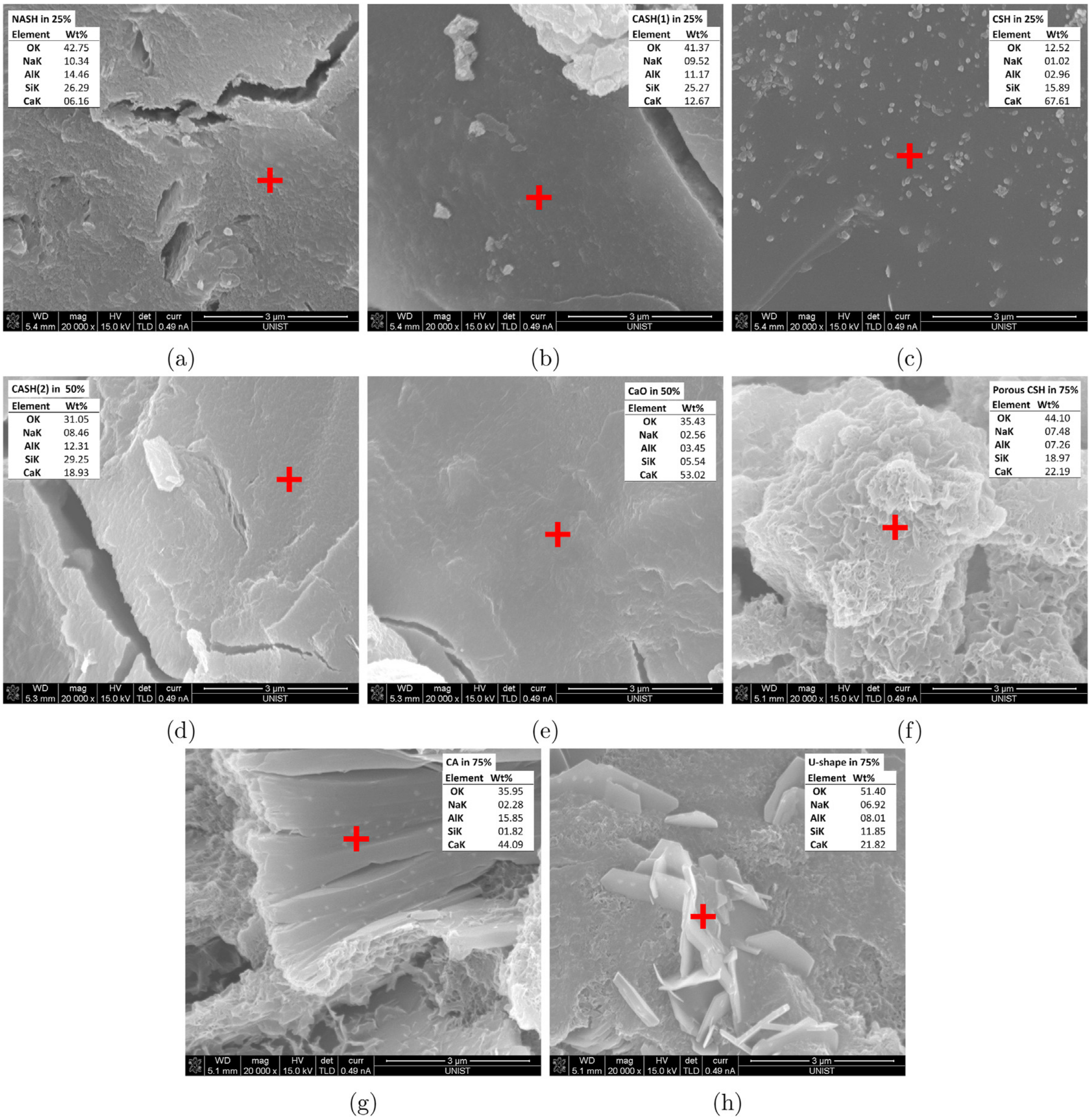


Fig. 10 – SEM images and EDS mapping results of the HACCs synthesized with the S/A 1.8 geopolymer and the w/c 0.48 cement paste of different mixing proportions: (a) 25% (geopolymer), (b) 50%, and (c) 75%.

strength of the HACC with the S/A 1.8 geopolymer is improved from 7 days to 28 days. The HACC with an S/A ratio 1.4 has the same degree of weight loss at 7 and 28 days, and the compressive strength does not increase. The HACC with an S/A ratio of 1.0 has a larger weight loss at 28 days than at 7 days, which can be attributed to a higher degree of hydration, and the compressive strength does not increase. This implies that the HACC with an S/A ratio of 1.0 may have more hydration phases than other HACCs.

3.4. SEM

Fig. 10 shows the SEM images and EDS mapping results of the HACCs synthesized with the S/A 1.8 geopolymer and the w/c 0.48 cement paste of different mixing proportions from 25% to 75%. Notably, the images of 0% (geopolymer) and 100% (cement paste) are not included because they have been shown in the previous studies [53,54]. Fig. 11 shows the detailed images of the spot marked in Fig. 10. All of the specimens are cured for 28 days. The overall Ca content in HACC increases as the mixing proportion of cement paste increases. Both N-A-S-H and C-A-S-H gels are observed in the 25% HACC, whereas C-A-S-H gels are the main structure of the 50% HACC. The failure in the observation of an N-A-S-H gel in the 50% HACC complies with the TGA results; the weight loss of the 50% HACC up to 200 °C is similar to that of the cement paste, which indicates that the weight loss from N-A-S-H gels is negligible. The N-A-S-H gels contain wedge-like pores on their surface, as shown in Fig. 11a, and the C-A-S-H gels look solid, as shown in Fig. 11b. The existence of C–S–H and CaO phases is confirmed in the 25% and 50% HACCs. The CaO possibly comes from free CaO in OPC, or it can originate from a chemical reaction as the CaO in Fig. 10b seems to be chemically bound to C-A-S-H gels. The 75% HACC has various Ca phases. It shows a porous C–S–H, a Ca aluminate phase, and an U-shape phase, which have been also observed in an HAC



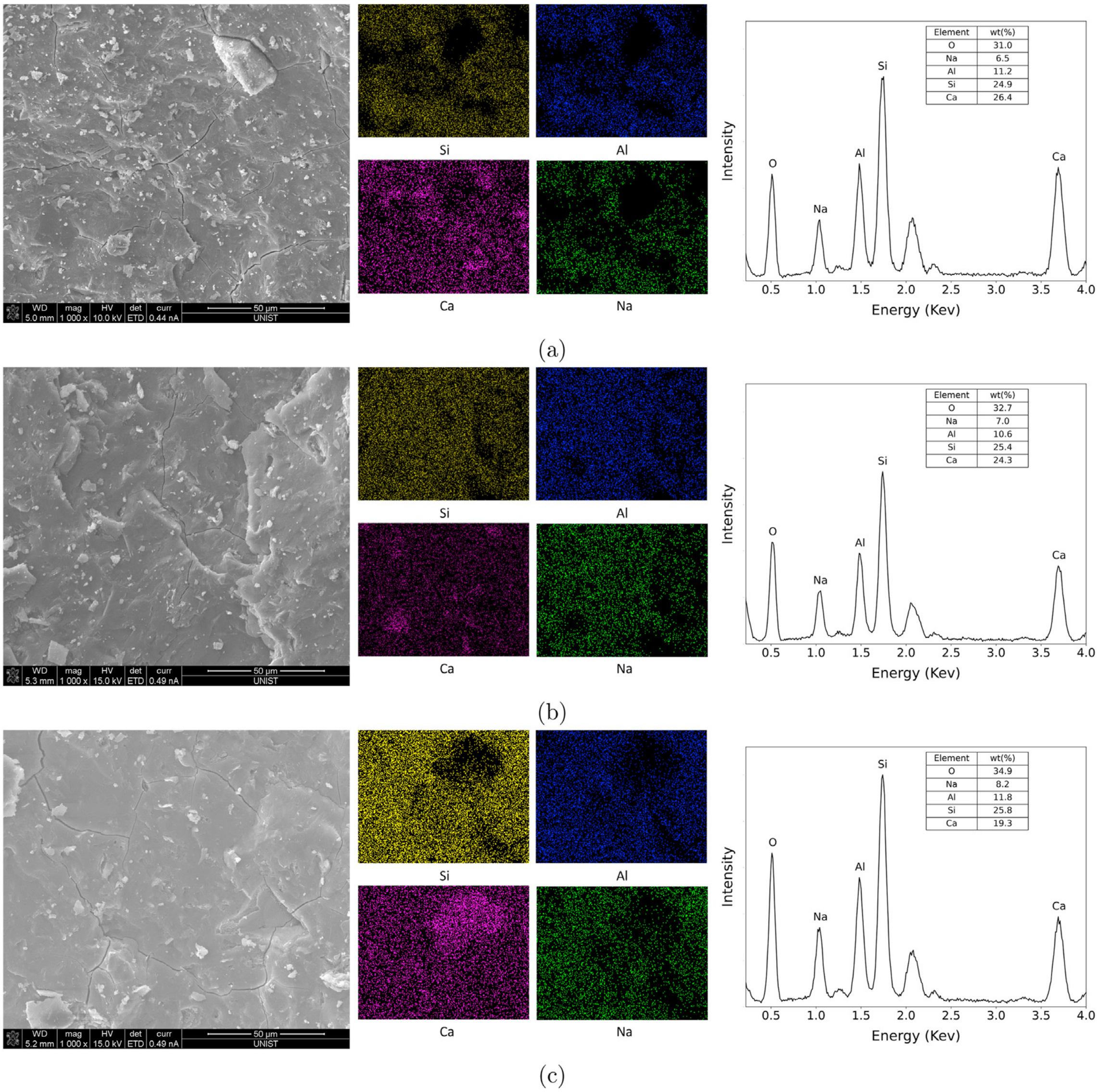
(a) (b) (c)
(d) (e) (f)
(g) (h)

Fig. 11 – Detailed SEM images of the spots marked in Fig. 10: (a) NASH gel in 25%, (b) C-A-S-H gel in 25%, (c) C–S–H in 25%, (d) C-A-S-H gel in 50%, (e) CaO in 50%, (f) porous C–S–H in 75%, (g) CA phase in 75%, and (h) U-shape phase in 75%.

with an alkaline activate solution in a previous study [24]. The alkaline solution induces porous C–S–H in cement paste. The lowest compressive strength of the 75% HACC can be attributed not only to the porous C–S–H but also to the inhomogeneity of the structure. The 50% HACC, on the contrary, has a homogeneous structure of C-A-S-H gels, and the homogeneity of the structure can be a key for the higher compressive strength of HACC.

Fig. 12 shows the SEM images of the 50% HACC synthesized with an S/A ratio of 1.8 geopolymer and the cement pastes of w/c ratios of 0.36, 0.42, and 0.48. No major differences among the 50% HACCs of different w/c ratios are observed similar to the TGA results, although the effect of the w/c ratio of cement paste on the compressive strength of HACC is considerable, as shown in Fig. 3. Some of the porous C-A-S-H gels are observed in the 50% HACC with a w/c ratio of 0.36; however, it is difficult to conclude that this is the main reason for the lower compressive strength. The 50% HACCs include C-A-S-H gels, C–S–H, and CaO phase; however, N-A-S-H gels are difficult to find. The TGA results demonstrate that the content of N-A-S-H gels can be minimal in the 50% HACC.

Fig. 13 shows the SEM images of the 50% HACCs synthesized with the w/c 0.48 cement paste and the geopolymer with S/A ratios of 1.0, 1.4, and 1.8. Fig. 14 shows detailed images of the spot marked in Fig. 13. A higher S/A ratio increases the homogeneity of the 50% HACC structure; although the Ca content in the HACCs are similar to each other, the Ca mapping results show that Ca in a lower S/A ratio seems more agglomerated. In the 50% HACC with an S/A ratio of 1.0, NASH gels and Ca phases are tangled with each other, as shown in Fig. 14a and b. Zeolite also exists near NASH gels, which is observed in the geopolymer with a low S/A ratio [46,53]. In the



(a)

Element	wt(%)
O	31.0
Na	6.5
Al	11.2
Si	24.9
Ca	26.4

(b)

Element	wt(%)
O	32.7
Na	7.0
Al	10.6
Si	25.4
Ca	24.3

(c)

Element	wt(%)
O	34.9
Na	8.2
Al	11.8
Si	25.8
Ca	19.3

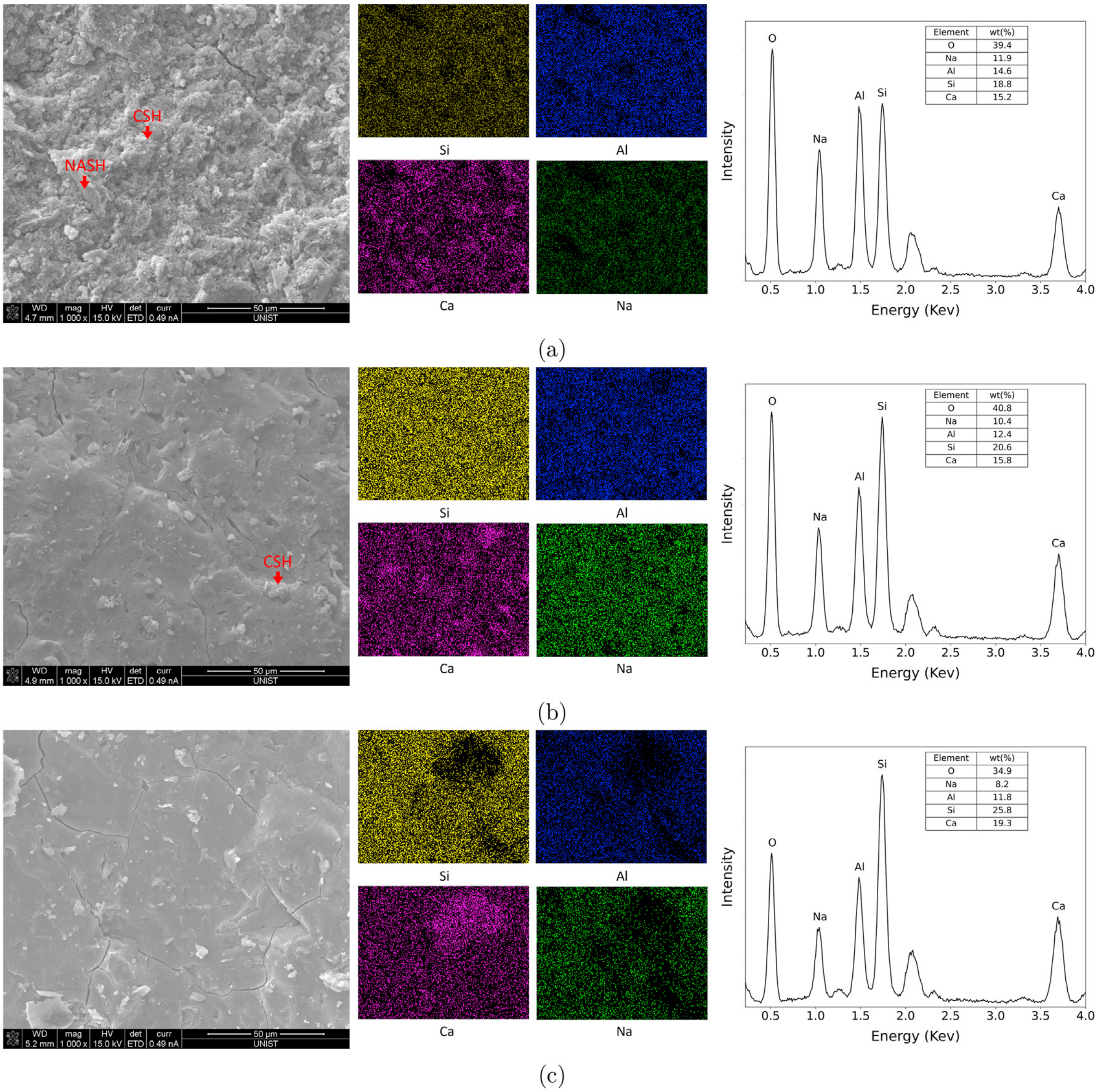
Fig. 12 – SEM images and EDS mapping results of the 50% HACCs synthesized with the S/A 1.8 geopolymer and the cement paste with different w/c ratios of: (a) 0.36, (b) 0.42, and (c) 0.48.

50% HACC with an S/A ratio of 1.4, the C-A-S-H gels take the main part of the HACC structure, yet C–S–H particles are still observed. As a result, an appropriate amount of sodium silicate is essential to merge NASH gels and cement paste to create C-A-S-H gels in HACC [17,55].

4. Concluding remarks

This paper presents the characteristics of materials synthesized with a geopolymer and cement paste with various mixing proportions over general dosages. The mixing proportion of OPC has been limited to a certain level because it significantly decreases the flow of the fresh mixture. Therefore, the particular mixing method involving the addition of OPC into geopolymer was adopted; a part of the initial mixing water was mixed with cement, and cement paste is added into geopolymer. This method resolved the flow decrement issue of the mixture of geopolymer and cement paste, and its compressive strength and the initial setting time were compared with various mix designs. The experimental variables were the mixing proportion of cement paste, the w/c ratio of cement paste, and the S/A ratio of geopolymer. The TGA and SEM tests were accompanied to examine the effect of the variables on the chemical structure of the mixture. This paper proposes the name of the mixture as HACC, as it contains some unique properties compared with traditional geopolymer and cement paste. The important findings are summarized below:

1. Cement paste improves the compressive strength of geopolymer, whereas geopolymer decreases the compressive strength of cement paste. As the mixing proportion of cement paste increases up to 50%, the C-A-S-H gels become



(a)

Element	wt(%)
O	39.4
Na	11.9
Al	14.6
Si	18.8
Ca	15.2

(b)

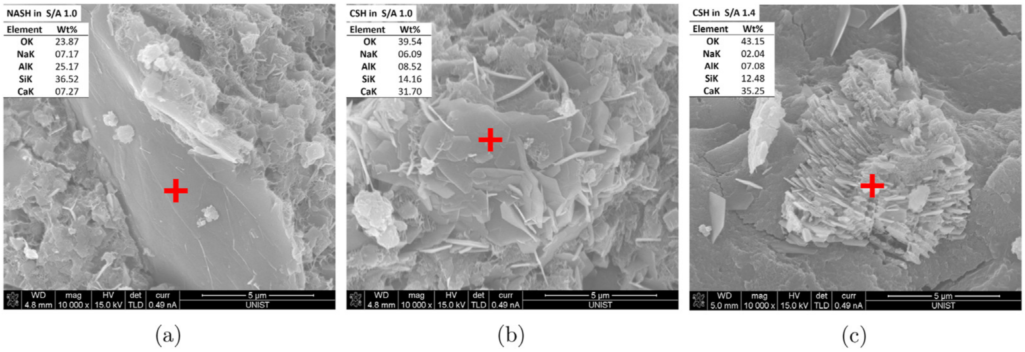
Element	wt(%)
O	40.8
Na	10.4
Al	12.4
Si	20.6
Ca	15.8

(c)

Element	wt(%)
O	34.9
Na	8.2
Al	11.8
Si	25.8
Ca	19.3

Fig. 13 – SEM images and EDS mapping results of the 50% HACCs synthesized with a w/c ratio of 0.48 cement paste and the geopolymer with different S/A ratios of: (a) 1.0, (b) 1.4, and (c) 1.8.

a main part of HACC structure, resulting in a more homogeneous formation. The 75% mixing proportion yields the lowest compressive strength, and it contains various Ca phases, such as porous C–S–H, Ca alumina phase, and U-shape phase. As a result, the 50% mixture generally exhibits the highest 28-day compressive strength.



NASH in S/A 1.0

Element	Wt%
OK	23.87
NaK	07.17
AlK	25.17
SiK	36.52
CaK	07.27

CSH in S/A 1.0

Element	Wt%
OK	39.54
NaK	06.09
AlK	08.52
SiK	14.16
CaK	31.70

CSH in S/A 1.4

Element	Wt%
OK	43.15
NaK	02.04
AlK	07.08
SiK	12.48
CaK	35.25

Fig. 14 – Detailed SEM images of the spots marked in Fig. 13: (a) NASH gel in S/A 1.0, (b) C–S–H in S/A 1.0, and (c) C–S–H in S/A 1.4.

2. The w/c ratio of cement paste is a critical factor for the compressive strength of the mixture. A low w/c ratio does not guarantees a higher compressive strength of HACC, which is extraordinary, as the compressive strengths of both geopolymer and cement paste decrease with the increase of the initial mixing water. The effect of the w/c ratio the initial setting time of HACC is not as significant as the compressive strength.
3. The S/A ratio of geopolymer is also an important variable for both the compressive strength and initial setting time of the mixture. Especially, the presence of sodium silicate helps N-A-S-H gels and cement paste phases merge, creating a homogeneous structure. As C-A-S-H gels become a main part of HACC, the compressive strength increases. Therefore, the usage of a proper S/A ratio is critical. Sodium silicate plays an important role in the reduction of the setting time. This indicates that the chemical reaction between sodium silicate and cement paste should be related to the fast setting time of HACC. Hence, the fast set of the HACC is caused by the combination of the reactions of Ca with geopolymer and sodium silicate with cement paste.
4. The TGA results confirm that HACC does not have portlandite after 7 days of curing. Therefore, the transformation of portlandite can induce a higher compressive strength of HACC than those of geopolymer and cement paste, filling voids inside. The TGA results also reveal that strength development of HACC from 7 days to 28 days is related to the further reaction of N-A-S-H gels. The OH groups in N-A-S-H gels condense resulting in the less total weight loss in TGA at 28 days.

Consequently, the extreme mixing proportion of Ca in geopolymer provoked the exceptional characteristics; the initial setting time is less than 10 min, and the 28-day compressive strength is higher than 80 MPa by the 50% HACC synthesized with the S/A 1.8 geopolymer and the w/c 0.48 cement paste. The overall water-to-solid ratio of the mixture is 0.46, and the fresh material was highly flowable as a self-consolidating mixture. The HACC is expected to be applied for creating foamed material because the fast setting is beneficial to trap air inside. Although mixtures of various mix designs were tested to reveal the effect of the basic mix design variables, several questions on the following issues still remain: i) life-cycle cost analysis on the HACC with a higher OPC content, ii) the reason for the w/c ratio significantly affecting the compressive strength of HACC, iii) the principle of fast setting and how to control it, and iv) long-term durability or other mechanical performances.

Among these questions, the most intriguing aspect is the chemical reaction mechanism of HACC, specifically, the disappearance of portlandite in the mixture. Portlandite or CH is a weak phase compared with C–S–H, and it is where pozzolanic material plays an important role in improving the performance of concrete by transforming CH to C–S–H. However, the pozzolanic reaction is usually slow, taking over a couple of months, and the options to accelerate the reaction speed are very few, namely, heat treatment, the grinding of pozzolanic material, or the application of higher reactive material. However, in the case of the HACC, even the 7-day curing specimens without heat treatment do not have any portlandite. If the chemical reaction mechanism of the mixture is fully studied, and if another practical method to accelerate the pozzolanic reaction can be discovered, more of pozzolanic material can be used in concrete without degradation of the early and late compressive strength of concrete.

Declaration of Competing Interest

The authors declare that they have no conflicts of interests.

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