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Characterization of a sodium aluminate($NaAlO_2$)-based accelerator made via a tablet processing method

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When an accelerator that is used in shotcrete reacts on cement, it quickly sets upon early hydration. Use of cold-weather concrete prevents concrete damage from freezing. There is difficulty securing workability, however, since early hydration makes it react rapidly. In this study, a tablet that is used in pharmaceuticals was made of an aluminate-based accelerator and is discussed in terms of its mortar setting time and flow test result. Also, the rate and progress of its hydration were evaluated by analyzing the X-ray diffraction (XRD) and scanning electron microscopy (SEM) results. As a result, in the sample that included both the tablet and the aluminate-based accelerator, hydrates such as calcium aluminate hydrate (C-A-H) and calcium hydroxide [$Ca(OH)_2$] were formed within similar times.

Key words: Tablet, Aluminate-based accelerator, C-A-H, Early strength, Workability.

Introduction

The reaction of cement with water forms hydrates that induce setting and hardening. Therefore, there is a very close link between hydration and hardening. The hydration of cement consists of compound compositions, the mechanism of which has been extensively studied [1]. An accelerator, which is mainly used in shotcrete, quickly reacts with the hydration. It has advantages in concrete in terms of preventing early frost damage and developing an early strength. In particular, the aluminate-based accelerator is applied due to the low deterioration of the long-term strength of a cement containing it. The chief ingredient of the aluminate-based accelerator is sodium aluminate ($NaAlO_2$). Sodium hydroxide (NaOH) and aluminum hydroxide [$Al(OH)_3$] are generated by hydrolysis, as shown below [2]:

$$4NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3 \quad (1)$$

NaOH breaks the low-molecular-weight calcium silicate hydrate (C-S-H) film, which is made around cement particles from C_3S and C_2S's early hydration, and helps promote the hydration. $NaAlO_2$ reacts with $Ca(OH)_2$, and in this stage, C-A-H is rapidly made [3, 4]:

$$3Ca(OH_2) + 2\ Al(OH)_3 \rightarrow 3CaO \cdot CAl_2O_3 \cdot 6H_2O \quad (2)$$

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In cold-weather concrete, the most important problem is the early frost damage caused by water freezing in the initial hardening stage, which has a bad influence on the strength and frost resistance after hardening of the concrete. To prevent early frost damage, an accelerator can be used. Workability is difficult to achieve, however, because the early hydration of accelerators makes them react rapidly, and it is difficult to secure an operation time [5, 6].

In this study, the process of tablet manufacturing via direct compression is as shown in Fig. 1. To adjust the initial reaction time and the operation time, the tablet was processed as shown in Fig. 1 [7, 8]. It was confirmed that such tablets secure the operation time by adjusting the reaction time and develop early strength to prevent early frost damage.

To achieve the goals of this study, flow tests and the mortar setting times were measured according to the elapsed times. Also, the rate and progress of the hydration were evaluated by analyzing the XRD and SEM result at the initial set, the final set, and after 24 h (for the strength to prevent early frost damage).

Experimental

The tablet of the powdered aluminate-based accelerator (PAA) was fabricated using a tablet press-making machine. It was cylindrical in shape and was 5 mm long, with a 5 mm diameter. Table 1 shows the features of the PAA tablet.

The mortar specimens were made with 5 levels according to ISO 697. The flow test and setting time were measured depending on the elapsed time. Also, the concrete

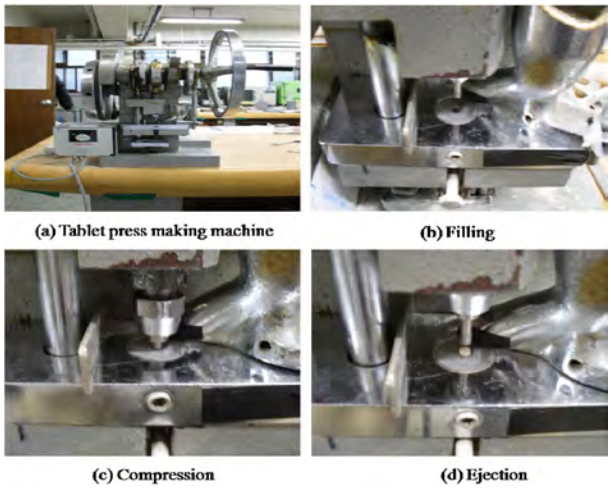

Fig. 1. Tablet processing method.

Table 1. Features of the powdered sodium aluminate-based accelerator (PAA) and Tablet.

powdered aluminate-based accelerator (PAA)	Tablet-shaped aluminate-based accelerator
Specific gravity: 1.45 g/cm^3 pH: 13, Appearance: Powder, Hue: White Main ingredient: Sodium aluminate ($NaAlO_2$)	Shape: Cylindrical Diameter: 5 mm Length: 5 mm

Table 2. Mixture proportions.

Type	Replacement Ratio
Mortar W/C = 0.5; Cement-to-sand ratio = 1:3	Control PAA: 0.5%; Tablet (0.5%, 1.0%, 1.5%, and 2.0%)
Concrete W/C = 52.0%; S/a = 48.5% (Binder: 337 kg/m^3)	Control PAA: 0.5%; Tablet (0.5%, 1.0%, 1.5%, and 2.0%)

specimens were made with 5 levels, such as in mortar, to confirm an early-strength improvement. Concrete mixtures were found in the pilot test, and the type and replacement ratio of each mixture are shown in Table 2.

When water was added to the cement, it gradually lost its workability with slight heating, and then it hardened because a new matrix was developed by the cement clinker that reacted with the water. This step is called setting. The hardening after the end of the setting is a step on the development of the measurable strength [9, 10].

After the curing at 15 ± 2 °C in a temperature and humidity chamber (Fig. 2), the penetration resistance was measured depending on the elapsed time. Then the setting time was measured according to the graph of the curved hand-fitting that was drawn after points were indicated using the penetration resistance and the elapsed time (The initial and final setting times were decided at the penetration resistance 3.5 and 28 MPa, respectively). Also, the compressive strengths were checked

Fig. 2. View of the specimens in chamber.

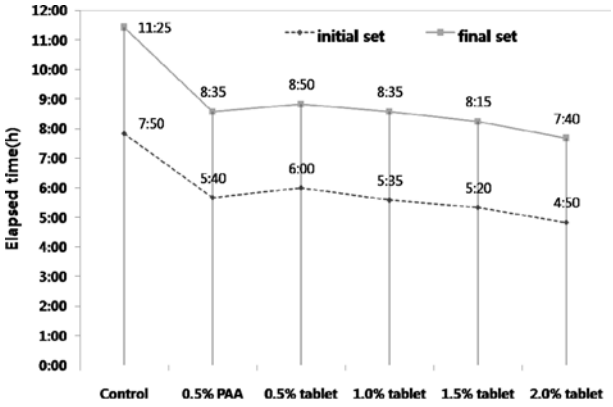

Fig. 3. Setting time.

after 14, 18, and 24 h to see if they matched the minimum compressive strength of 5 MPa for early-frost prevention, according to ASTM C 39 [11].

The reaction of cement with water forms various hydrates. The compound of the cement clinker, which has a significant impact on the setting, is C_3A, because it sets the cement rapidly since C-A-H has a rapid increase in the early hydration stage. The strength development is mainly described through the matrix and structure of the formed C-S-H phase, because the C-S-H formed, which is the progress by time, decreases the pores of the cement paste [12]. The admixture for promoting such reactions is the aluminate-based accelerator. In this study, after the hydration progress was stopped with acetone after the initial setting, the final setting, and 24 h, sampling was conducted. The rate and progress of the hydration of the tablets were evaluated by analyzing the XRD and SEM results.

Results and Discussion

In Fig. 3, the initial and final setting times were shortened depending on the increased replacement ratio of the tablets, because the main ingredient of the tablet was PAA. It was directly involved in the hydration and setting of the cement. The setting results of the 1.0% tablet sample were similar to those of the 0.5% PAA. Unlike the recent research on accelerators, however, the setting time depending on the tablet increment was not significantly shortened. This is thought to have been due to the slow reaction of the cement and the large tablets due to the increased quantity of the tablets.

A cement clinker typically consists of an alite (C_3S),

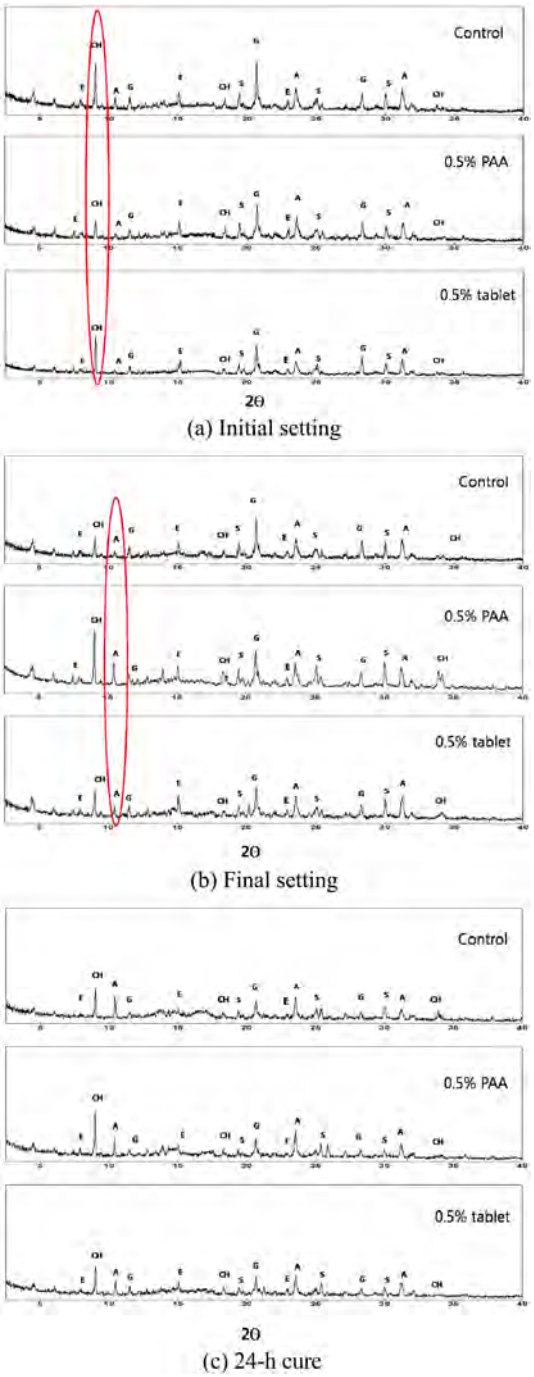

Fig. 4. XRD patterns in terms of the setting time and the 24-h cure [S : C-S-H, A : C-A-H, E : Ettringite, G : Gypsum, CH : $Ca(OH)_2$].

belite (C_2S), aluminate (C_3A), and ferrite (C_4AF). When these compositions react with water, the unstable calcium hydrates stabilize. Among them, C_3S and C_2S form low-molecular-weight C-S-H and $Ca(OH)_2$, as follows [13]:

$$2C_3S + 6H_2O \rightarrow C_3S_3H_3 + 3Ca(OH)_2 \quad (3)$$
$$2C_2S + 4H_2O \rightarrow C_3S_2H_3 + Ca(OH)_2 \quad (4)$$

If an aluminate-based accelerator, the chief ingredient of which is sodium aluminate ($NaAlO_2$), is put into the cement and water, sodium hydroxide (NaOH) and aluminum hydroxide [$Al(OH)_3$] will be generated via hydrolysis. Also aluminum hydroxide [$Al(OH)_3$], which reacts with $Ca(OH)_2$, rapidly forms C-A-H [14]. In Fig. 4 (a), the $Ca(OH)_2$ peak of the PAA 0.5% is smaller than that of the control, and the $Ca(OH)_2$ peak of the 0.5% tablet sample is higher than that of the 0.5% PAA, because the control formed much more $Ca(OH)_2$ than did the PAA due to the general hydration and the 0.5% PAA considerably consumed the $Ca(OH)_2$ through its reaction with the $Al(OH)_3$. On the other hand, it is thought that the 0.5% tablet sample only slightly consumed $Ca(OH)_2$ due to it adjusting the reaction time.

C_3A sets cement rapidly, since C-A-H rapidly increases the early hydration [15]. Fig. 4 (b) shows that the C-A-H peaks of the 0.5% PAA and the 0.5% tablet sample are higher than that of the control, which indicates that the setting time was shortened due to the increased C-A-H. Fig. 4 (c) shows the hardening in progress, since all the cases showed similar XRD patterns. In particular, the setting of the 0.5% tablet sample was not significantly shortened at the early hydration stage and after the time elapsed, it confirms that the setting time was shortened.

Fig. 5 shows the observed results in terms of the hydration state via SEM in the initial setting, final setting, and 24-h cured. Low-molecular-weight C-S-H and $Ca(OH)_2$ were formed around the cement particles at the early hydration [16]. Fig. 5 (a) shows that in the control, 0.5% PAA, and 0.5% tablet sample, a low-molecular-weight C-S-H with a chestnut morphology and the $Ca(OH)_2$ with a hexagonal tubular morphology were formed around the cement particles. Among these, the 0.5% PAA showed the smallest amount of $Ca(OH)_2$ formed. If the hydration progressed further, a membrane-shaped C-S-H will be formed around the particles. This membrane will be dense, since it will become thick both inside and outside the particles over time. Fig. 5 (b) shows such a denser state than that in Fig. 5 (a). Also, the 0.5% PAA and the 0.5% tablet sample were denser than the control.

The strength development may be progressed due to a reduction of the pores that filled the hydrates. If the C-S-H and $Ca(OH)_2$ around the particles encounters other similar particles during the progress, such progress will be stopped. The overall volume increases, however, if ettringite is formed from aluminate (C_3A) and ettringite makes space by pressure if there is not enough space. Therefore, the strength will be developed since hydrates such as C-S-H fill the spaces [17, 18]. Fig. 5 (c) shows microstructures of early-strength development. It especially shows that the ettringite of the long slender needles had filled the spaces depending on the hydration progress. Also, the control had more pores than the 0.5% PAA and the 0.5% tablet sample, and less ettringite than the 0.5%

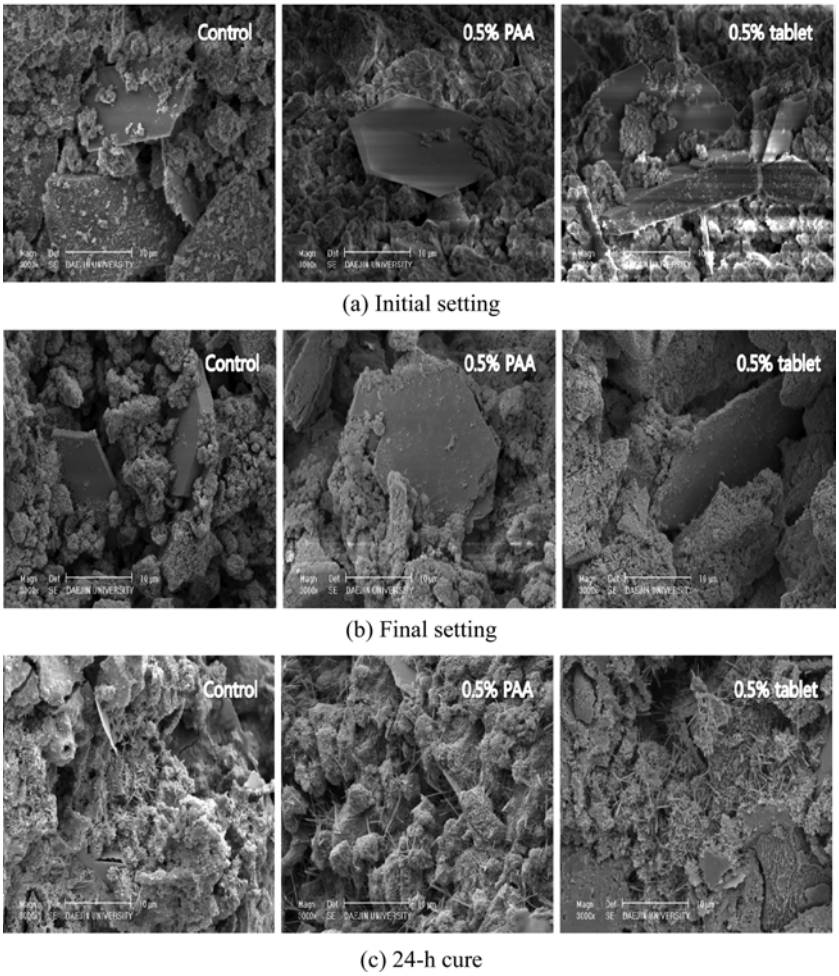

Fig. 5. SEM micrographs of the hydrates based on the setting time and 24-h cure.

Table 3. Slump and early-compressive-strength measurement results.

Type	Flow (mm)			Compressive Strength (MPa)		
	0	30 mins	60 mins	14 hrs	18 hrs	24 hrs
Control	162	158	146	2.0	3.2	4.2
0.5% PAA	148	125	105	3.1	4.7	6.3
0.5% tablet	165	158	146	3.2	4.5	6.2
1.0% tablet	161	156	146	2.9	4.1	5.7
1.5% tablet	160	153	140	2.4	3.9	5.3
2.0% tablet	163	157	144	2.2	3.8	5.5

PAA and the 0.5% tablet sample.

The test results of the tablets to confirm the possibility of securing workability and developing early strength are shown in Table 3.

In Table 3 and Fig. 6, the loss of all the mixtures, except for those of the control, did not significantly change with the elapsed time. In the case of the tablets, it showed the possibility of securing workability during the operation time. In contrast, the 0.5% PAA sample had similar research results due to the measured low flow immediately after the mixture. The rate of the

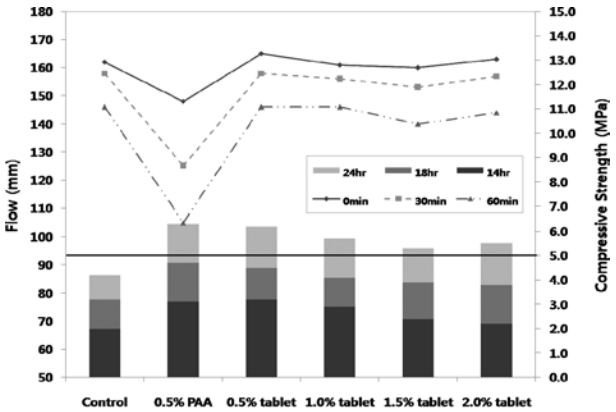

Fig. 6. Flow and early compressive strength.

hydration and hydrates for the early strength development was confirmed by the XRD and SEM analysis results. Fig. 6 shows that all the mixtures, except for the control, meet the minimum compressive strength standard of 5 MPa for early-frost prevention at 24 h, but a rise in strength development was anticipated depending on the increased tablet replacement, and high-replacement mixtures were measured in the lower than 0.5% tablet sample, because they formed much C-A-H which retarded the

hydration of C_3S and C_2S for the strength development even if the setting time was shortened by C-A-H in the early hydration stage [19, 20]. Moreover, there might have been a non-reacting tablet in the concrete, as the tablet was large.

Summary

Tablets were fabricated to secure the workability of an aluminate-based accelerator. Also, the rate of hydration and hydrates of the tablet was determined to develop its early strength through a test and analysis. The conclusions are as follows.

(1) In the setting test, the setting time with the tablet was shortened, as with the powdered aluminate-based accelerator (PAA).
(2) In the XRD analysis, the tablet only slightly consumed the calcium hydroxide [$Ca(OH)_2$] via its reaction with aluminum hydroxide [$Al(OH)_3$] in the early hydration stage. After time elapsed, the XRD patterns confirmed that the setting-time was shortened due to the increased amount of C-A-H.
(3) The results of the SEM analysis showed that the tablet's rate of hydration and hydrates for the development of its strength and dense state was similar to that of the PAA sample
(4) The workability and strength results for the early-frost prevention showed that the workability of all the mixtures with the tablets did not significantly change with the elapsed time and met the minimum compressive strength of 5 MPa for early-frost damage prevention.

Therefore, it was found that it is possible to secure workability for a tablet in time, and to develop its early strength to prevent early frost damage in cold weather.

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