

Journal of Materials and Construction ISSN 2734-9438

Website: www. jomc.vn

Effect of calcium acetate on some properties of blended portland cement

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KEYWORDS

Calcium acetate Blended Portland cement Compressive strength Heat of hydration **Properties**

ABSTRACT

The objective of this study is to evaluate the influence of calcium acetate (CA) content on certain properties of blended Portland cement. The investigated CA dosages were 0%, 0.3%, 0.6%, and 1.0%. The properties examined include water of consistency, setting time, heat of hydration during the first 24 hours, compressive strength at 1, 3, 7, and 28 days, and soundness. The results indicate that increasing CA content from 0% to 1.0% reduces the water of consistency by approximately 2%. While CA has a negligible effect on the initial setting time, it shortens the final setting time by around 20 minutes. An increase in CA content accelerates the early-stage hydration rate but subsequently leads to a reduction in both the peak temperature and the total heat released within the first 24 hours. CA adversely affects the 1-day compressive strength; however, it slightly enhances strength at 3 and 7 days when used at 0.3% and 0.6% dosages. A significant improvement in 28-day compressive strength is observed, particularly at 0.6% CA, which yields the highest enhancement (an increase of 23.8% compared to the control sample). CA does not significantly impact the soundness of the cement, and all tested samples satisfy the requirements of TCVN 6260:2020. Based on the findings, a CA dosage of 0.6% appears optimal, as it minimizes 1-day strength reduction while providing superior strength development at later ages (3, 7, and 28 days) compared to the 0.3% and 1.0% CA mixtures.

1. Introduction

Cement production is known to emit a substantial amount of CO₂, ranging from 0.7 to 1.1 tons of CO₂ per ton of cement produced [1-3]. To mitigate these emissions, cement plants commonly incorporate mineral additives as partial clinker replacements [4, 5]. These mineral additives include both inert fillers and reactive supplementary cementitious materials (SCMs). Their utilization not only contributes to environmental sustainability but also reduces production costs and enhances the properties of cement. Limestone is a widely used filler. When used at appropriate dosages and fineness, it improves the particle packing of the cement, thereby enhancing properties of mortar and concrete such as workability and strength [6, 7].

Reactive SCMs such as basalt powder, fly ash, bottom ash, and ground granulated blast furnace slag (GGBFS) are also frequently used. During the hydration process, the active components of these additives, mainly SiO₂ and Al₂O₃, react with Ca(OH)₂ released from the hydration of Portland clinker to form C-S-H and C-A-H gels [8]. These reactions refine the microstructure of the hardened cement paste and improve various performance attributes of cement and concrete, including enhanced long-term strength, increased sulfate resistance, reduced heat of hydration, mitigation of alkali-silica reaction, and improved chloride resistance [9-11].

However, the use of SCMs typically results in reduced early-age strength, and in some cases, even the 28-day strength may decline if high replacement levels are used. This poses a limitation on the maximum allowable clinker replacement in cement. Several studies have indicated that early strength development can be improved by incorporating hydration accelerators [12-15]. Calcium chloride (CaCl₂) has long been used as a highly effective accelerator for both early and later strength gains in cementitious systems [14]. However, its application is restricted in reinforced concrete due to its corrosive effect on steel reinforcement [12].

Recent studies have reported that calcium acetate (CA) can improve the compressive strength and certain properties of cement without inducing corrosion in steel reinforcement. The effect of CA on cement performance is highly dependent on its dosage. Compressive strength typically increases with CA content up to an optimal level, beyond which strength begins to decline [16-20]. The optimal dosage varies depending on the type of cement. At certain dosages, CA can enhance both early and later strength, whereas at other dosages it may improve early strength but reduce long-term strength [16-18, 20].

Numerous studies have demonstrated that CA promotes the early hydration of C₃A and C₃S, resulting in increased formation of hydration products such as ettringite, CH, C-S-H, and C-A-S-H gels [17, 18]. These products help fill the capillary pores, reducing overall porosity. However, excessive CA content may lower the pH of the paste and introduce acetic acid, which can retard hydration and reduce strength.

CA has been reported to reduce the water of consistency and enhance the flowability of mortar mixes [16-18]. Its effect on setting time varies depending on its dosage and the type of cement. El-Didamony et al. [16], working with a blended cement (80% OPC + 20% silica fume), observed that CA dosages from 0 to 2.5% reduced both initial and final setting times. Kim et al. [17], in a study using OPC,

reported that CA additions from 0 to 3% shortened the initial setting time, but the final setting time showed mixed trends (1% reduced it, 2% had no effect, and 3% increased it). Similarly, Cao et al. [18] observed that with 1% and 2% CA, both initial and final setting times decreased, while at 3% CA, they increased beyond that of the control sample.

Compared to conventional accelerators such as calcium chloride (CaCl₂) and calcium nitrate (Ca(NO₃)₂), calcium acetate (CA) offers the advantage of being non-corrosive to steel reinforcement, making it more suitable for reinforced concrete applications. While CaCl2 is highly effective and inexpensive, its use is restricted due to its potential to cause corrosion. Calcium nitrate is less corrosive but generally more costly and less readily available in some regions. Calcium acetate, therefore, presents a promising alternative in terms of safety and compatibility.

While the use of mineral additives is well recognized for reducing CO₂ emissions by lowering clinker content, the environmental impact of using chemical admixtures such as calcium acetate (CA) is less documented. Although CA does not directly reduce clinker content, its ability to enhance compressive strength may allow for further optimization of blended cement formulations, potentially enabling a higher proportion of mineral additives without compromising performance. A preliminary estimation indicates that increasing the replacement of clinker by 5-10% with mineral additives—made feasible by strength-enhancing admixtures like CA—could reduce CO₂ emissions by approximately 40-80 kg per ton of cement, depending on the clinker factor and energy source.

To date, no comprehensive study has been conducted to evaluate the effects of CA on the hydration and performance of blended Portland cement incorporating multiple types of mineral additives. Therefore, the objective of this study is to assess the influence of CA content (ranging from 0% to 1%) on selected properties of blended Portland cement. The investigated properties include water of consistency, setting time, heat of hydration during the first 24 hours, compressive strength at 1, 3, 7, and 28 days, and soundness.

2. Materials and experimental procedure

2.1. Materials

The blended Portland cement used in this study was a commercially available PCB30 cement produced domestically. The composition of the cement is presented in Table 1, while the chemical and mineralogical compositions of the clinker are shown in Tables 2 and 3, respectively. CA was used as a commercially available laboratory-grade reagent, with a purity of $\geq 98\%$ Ca(CH₂COO)₂·H₂O.

Table 1. Composition of PCB30 cement.

| Component | Clinker | Gypsum | Limestone | Basalt | Bottom ash | Fly ash |
|-----------|---------|--------|-----------|--------|------------|---------|
| Ratio (%) | 65.5 | 3.0 | 9.7 | 11.0 | 6.8 | 4.0 |

Table 2. Chemical composition of the clinker.

| Oxide | SiO ₂ | Al_2O_3 | Fe_2O_3 | CaO | MgO | Na ₂ O | K ₂ O | SO_3 |
|-----------|------------------|-----------|-----------|-------|------|-------------------|------------------|--------|
| Ratio (%) | 21.96 | 5.53 | 3.33 | 65.25 | 1.92 | 0.11 | 0.63 | 0.39 |

Table 3. Mineralogical composition of the clinker (according to Bogue's method).

| Mineral | C ₃ S | C ₂ S | C ₃ A | C ₄ AF |
|-----------|------------------|------------------|------------------|-------------------|
| Ratio (%) | 50.4 | 27.4 | 9.0 | 10.1 |

2.2. Experimental procedure

Cement samples were prepared by weighing and proportioning the constituents as specified in Table 4. CA was first dissolved in water using a mechanical stirrer and mixed for 3 minutes to ensure uniform dispersion of the additive in the mixing water.

The water of consistency, setting time, and soundness of the cement samples were determined in accordance with TCVN 6017:2011 [21]. The compressive strength of the control and CA-modified cement mortar samples was evaluated following the procedure described in TCVN 6016:2011 [22].

The heat of hydration was determined as follows: Cement paste

samples (both control and CA-modified) were mixed using a laboratory mixer at low speed for 3 minutes. The fresh paste was then placed into cylindrical plastic containers (\emptyset 5 cm \times 4 cm), which were subsequently sealed inside insulated foam boxes. A thermocouple was inserted into the center of each sample and connected to a temperature-logging device. The internal temperature was automatically recorded every 30 seconds for a total duration of 24 hours.

Table 4. Composition of cement mixtures

| No. | Ratio of constituents (%) | | |
|-----|---------------------------|-----|--|
| | Cement | CA | |
| 1 | 100.0 | 0 | |
| 2 | 99.7 | 0.3 | |
| 3 | 99.4 | 0.6 | |
| 4 | 99.0 | 1.0 | |

Results and discussion

3.1. Water of consistency

The results of the water of consistency test for the cement samples are presented in Figure 1.

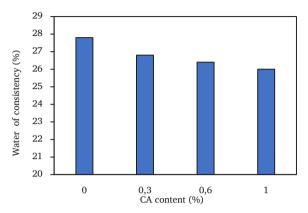


Figure 1. Water of consistency of cement samples.

As shown in Figure 1, all cement samples containing CA exhibited a lower water of consistency compared to the control sample. Moreover, an increase in CA content resulted in a further reduction in the water of consistency. Specifically, when the CA content increased from 0% to 1%, the water of consistency decreased by approximately 2%.

This reduction in water demand can be attributed to the dissociation of CA into Ca2+ and CH3COO- ions in the pore solution. These ions may be adsorbed onto the surface of cement particles, leading to the development of electrostatic repulsion between them [18]. This electrostatic repulsion helps to disperse the cement particles more effectively, thereby reducing flocculation and lowering the amount of water required to achieve workable paste consistency. Similar reductions in water demand with CA addition were also reported by El-Didamony et al. [16] and Kim et al. [17], who observed improved flowability and reduced water requirement in blended and ordinary Portland cement systems, respectively. These consistent findings support the interpretation that CA acts as a dispersing agent at low dosages, contributing to improved rheological behavior of cement pastes.

Setting time 3.2

The initial and final setting times of the cement samples were determined, and the results are presented in Figure 2.

As shown in Figure 2, the initial setting times of the CAcontaining samples were comparable to that of the control sample, indicating that calcium acetate (CA) had negligible influence on the onset of setting. However, CA significantly shortened the final setting time by approximately 20 minutes. All samples containing CA satisfied the requirements specified in TCVN 6260:2020 [23].

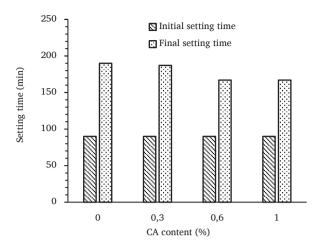


Figure 2. Setting times of cement samples.

The reduction in final setting time can be attributed to the accelerating effect of CA on the early hydration of C₃A and C₃S, which promotes the formation of ettringite, CH, and C-S-H [17, 18]. These hydration products contribute to the development of a solid skeleton, thus accelerating the setting process.

In addition, the decrease in water of consistency also contributes to the shortened setting time. A lower mixing water content leads to faster saturation of Ca(OH)₂ in the pore solution, promoting early crystallization of CH and accelerating the breakdown of the protective C-S-H layer on cement particles, further enhancing early hydration [24].

3.3. Heat of hydration

The results of the heat of hydration tests for cement samples containing varying dosages of CA are shown in Figure 3.

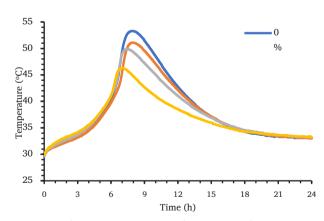


Figure 3. Temperature of cement samples.

As shown in Figure 3, increasing the CA content from 0% to 1% caused the peak of the hydration heat release curve to occur earlier, while the peak temperature decreased. Specifically, the peak shifted from approximately 8 hours in the control sample to around 7 hours in

the sample with 1% CA. The peak temperature also dropped from 53 °C in the control to 46.2 °C in the 1% CA sample.

These results indicate that while CA accelerates the onset of hydration, resulting in a faster initial reaction rate, the maximum temperature and total heat release over 24 hours are lower than those of the control. This can be attributed to the Ca²⁺ ions released by CA, which promote the early formation of hydration products such as calcium silicate hydrate (C-S-H) and ettringite [17, 18]. These hydration products form a dense layer around the cement particles, hindering further ingress of water and ions, thereby slowing the continuation of the hydration process and reducing the peak temperature. Moreover, acetate ions may adsorb onto the surface of cement particles and early hydration products, further inhibiting the progression of hydration reactions.

3.3. Compressive strength

The compressive strength results of the mortar samples at 1, 3, 7, and 28 days are presented in Figure 4.

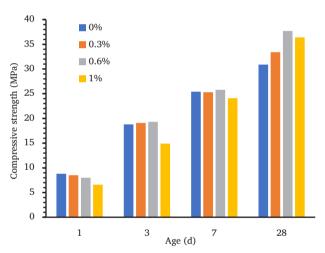


Figure 4. Compressive strength of cement mortar samples.

As shown in Figure 4, the 1-day compressive strength decreased with increasing CA content from 0 to 1%. The reductions compared to the control sample were approximately 3.4%, 8.7%, and 25.3% at CA dosages of 0.3%, 0.6%, and 1%, respectively. This trend corresponds well with the heat of hydration results, where the total heat released in the first 24 hours tended to decrease as CA content increased. The rapid early hydration promoted by CA forms a dense shell around cement particles, which subsequently inhibits further hydration.

At 3 and 7 days, the effect of CA became more positive. At 0.3% and 0.6% CA, the compressive strength slightly increased by about 2% compared to the control. At 1% CA, the compressive strength remained lower than the control, but the degree of reduction lessened—from a 20% decrease at 3 days to only a 5% decrease at 7 days. This strength gain indicates that CA partially reactivates hydration, producing more

hydration products and denser microstructures [17, 18]. However, higher CA contents reduce pH and inhibit cement hydration, resulting in lower compressive strength.

At 28 days, CA significantly improved mortar strength at all dosages. The sample containing 0.6% CA exhibited the highest increase in compressive strength (23.8%) compared to the control. These results suggest that CA strongly promotes late-stage hydration reactions, such as the hydration of C₂S and the pozzolanic reactions of active mineral admixtures. However, at high dosages (e.g., 1%), the increased concentration of acetate ions may lower the pore solution pH, thereby suppressing clinker hydration and diminishing the reactivity of some supplementary cementitious materials, ultimately limiting strength development.

3.4. Soundness

The results of soundness test for cement samples are presented in Table 5.

Table 5. Soundness of cement samples.

| No. | CA content (%) | Expansion (mm) |
|-----|----------------|----------------|
| 1 | 0 | 1.05 |
| 2 | 1 | 0.83 |
| 3 | 2 | 1.02 |
| 4 | 3 | 1.07 |

The results in **Table 5** indicate that the incorporation of CA does not significantly affect the expansion of the cement. All samples satisfied the requirement for soundness specified in TCVN 6260:2020 (<10 mm).

4. Conclusions

Based on the results obtained from the study of blended Portland cement samples incorporating CA at dosages of 0.3%, 0.6%, and 1%, the following conclusions are drawn:

- CA reduces the water of consistency of cement, with an approximate decrease of 2% as the CA content increases from 0% to 1%.
- CA has negligible effect on the initial setting time but significantly shortens the final setting time. When increasing CA from 0% to 1%, the final setting time decreases by approximately 20 minutes. All samples with CA meet the requirements of TCVN 6260:2020.
- The temperature profiles of cement pastes over the first 24 hours indicate that CA accelerates the early-stage hydration of cement, but subsequently reduces the hydration rate, resulting in a lower peak temperature and reduced total heat release.
- CA decreases 1-day compressive strength. However, at 0.3% and 0.6% CA, strength slightly improves at 3 and 7 days. At 1% CA, strength remains lower than the control but the reduction diminishes over time. At 28 days, all CA-containing samples show a clear

improvement in strength, with the 0.6% CA mixture achieving the highest increase (23.8% over the control).

- CA does not significantly affect the soundness of cement; all mixtures comply with the expansion limit specified in TCVN 6260:2020.

Among the tested dosages, 0.6% CA is considered optimal, as it minimizes 1-day strength loss and enhances compressive strength at 3, 7, and 28 days more effectively than the other dosages.

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