Comparison of Effects of Sodium Bicarbonate and Sodium Carbonate on the Hydration and Properties of Portland Cement Paste

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Abstract: Carbonates and bicarbonates are two groups of accelerators which can be used in sprayed concrete. In this study, the effects of the two accelerators sodium carbonate (Na\(_2\)CO\(_3\)) and sodium bicarbonate (NaHCO\(_3\)) (0%, 1%, 2%, 3%, and 4% by weight of ordinary Portland cement OPC) on the properties of OPC paste were compared. The results show that both of them could accelerate the initial and final setting time of OPC paste, but the effect of the two accelerators on the compressive strength were different. After 1 day, sodium bicarbonate at 3% had the highest strength while sodium carbonate at 1% had the highest strength. After 7 days, both of the two accelerators at 1% had the highest compressive strength. After 28 days, the compressive strength decreased with the increase of the two. The improved strength at 1 and 7 days was caused by the accelerated formation of ettringite and the formation of CaCO\(_3\) through the reactions between the two with portlandite. The decrease of strength was caused by the Na\(^+\) could reduce the adhesion between C-S-H gel by replacing the Ca\(^{2+}\). NaHCO\(_3\) was found be a better accelerator than Na\(_2\)CO\(_3\).

Keywords: NaHCO\(_3\); Na\(_2\)CO\(_3\); portland cement; compressive strength; setting time

1. Introduction

Rapid hardening ability and high early strength are essential properties for shotcrete or sprayed concrete. Different accelerators were usually used in order to meet these requirements [1–9]. The mostly used accelerators including alkali carbonates, alkali hydroxide, alkali silicate, and alkali aluminate. For example, the sodium silicate was found to be able to modify the ITZ between the cement paste and aggregates and decrease the porosity of mortar [10]. Sodium aluminate and potassium aluminate can accelerate the formation of ettringite in the cement paste, and thus cause a rapid hardening effect [11]. Sodium aluminate was reported to be able to modify the pore structure of cement paste at an early age, improve the resistance to chloride ingress, and increase early-age compressive strength [12]. Carbonates [7,13–17] and bicarbonates with alkali were also among the most-used accelerators, such as Na\(_2\)CO\(_3\) and NaHCO\(_3\) [18–22]. Mathur and Sharma [23] reported that the NaHCO\(_3\) can improve the strength and porosity of cement paste. Chandrawat and Yadav [24] found that the Na\(_2\)CO\(_3\) could enhance the compressive strength and durability of cement paste. The work of Kunther et al. [25] showed that the bicarbonate ions could reduce the expansion of mortar and improve the sulfate resistance of mortar when subjected to sulfate attack. Yang et al. [26] reported that the addition of NaHCO\(_3\) and calcium lignosulphonate together could accelerate the formation of ettringite in the fly ash cement paste by changing the liquid-phase composition and the status of ettringite crystallization. Jang et al. [20] showed that the addition of 1% and 2% NaHCO\(_3\) could accelerate the hydration of
cement paste and improve both flexural and compressive strength of the mortar specimen, but the addition of above 5% NaHCO$_3$ caused the adverse effect on the strength development because of the formation of strong alkali NaOH in the specimen. Reddy et al. [27], however, reported that the both of Na$_2$CO$_3$ and NaHCO$_3$ could decrease the compressive and tensile strength of concrete regardless of the content added or test age, and they also reported a significant reduction of strength after 28 days. However, Reddy and Krishna [28] reported that either Na$_2$CO$_3$ or NaHCO$_3$ could increase the early age strength at 3 and 7 days but decrease significantly the strength after 28 days, besides, they reported that Na$_2$CO$_3$ accelerated the setting time whereas the NaHCO$_3$ retarded the setting time. In addition, the structure and shape of the interface transition zone between the slurry and the aggregate in the cement composite material is a complicated problem. It has been well accepted that [29,30] the cement-based interface transition zone of the coarse aggregate is the weakest unit in the concrete, and the fly ash as mineral additive has a positive impact on the performance improvement of the interface transition zone.

It can be seen that there exist conflicted findings on the influence of Na$_2$CO$_3$ and NaHCO$_3$ on the setting time and physical properties of cementitious materials. It is necessary to carry out a comprehensive study on the effects of the two accelerators on the properties of cement paste and make a comparison between the two. In order to investigate and compare the effects of the two accelerators on the properties of OPC paste, the same amount of Na$_2$CO$_3$ and NaHCO$_3$ with 0%, 1%, 2%, 3%, and 4% weight of OPC were added into different mixes and the setting time and compressive strength at ages of 1, 7, and 28 days were studied, besides, the related hydration mechanism and hydration products were investigated through hydration heat, Thermogravimetry-Differential Thermal Analysis (TG-DTA), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM) tests.

2. Materials and Methods

2.1. Materials

P.O. 42.5 ordinary Portland cement (OPC) in accordance with a Chinese standard GB175-2007 [31] was used. The physical properties and chemical composition of OPC are shown Tables 1 and 2. The mineral composition of OPC is shown in Table 3. The NaHCO$_3$ and Na$_2$CO$_3$ used were in powder form and the purity was >99.5% and >99.8%, respectively. A superplasticizer used was polycarboxylate. The mixing water was deionized water.

| Fineness/% | Stability | Setting Time/min | Flexural Strength/MPa | Compressive Strength/MPa |
|------------|-----------|------------------|-----------------------|-------------------------|
|            |           | Initial          | Final                 | 3 days                  | 28 days                 |
| 1.5        | Qualified | 181              | 378                   | 5.1                     | 9.3                     | 25.3                    | 51.6                    |

| SiO$_2$  | CaO  | Al$_2$O$_3$ | Fe$_2$O$_3$ | MgO  | Na$_2$O | K$_2$O | LOI |
|----------|------|------------|------------|------|---------|-------|-----|
| 22.96    | 63.87| 5.73       | 3.31       | 2.64 | 0.32    | 0.23  | 0.18|

| C$_3$S   | C$_2$S | C$_3$A | C$_4$AF |
|----------|--------|-------|---------|
| 54.5     | 19.23  | 8.36  | 10.14   |

2.2. Methods

The mix design is shown in Table 4. Water-cement ratio (w/c) was kept same as 0.35. The superplasticizer was kept same as 0.5% by weight of OPC. OPC was firstly mixed with NaHCO$_3$
or Na$_2$CO$_3$ in dry state. The water and superplasticizer were then added and mixing speed was at 60 rpm for 2 min followed by 120 rpm for another 2 min. The weight of NaHCO$_3$ and Na$_2$CO$_3$ were added as 1%, 2%, 3%, and 4% by weight of cement in different mixes. Specimens were cured under standard curing condition (20 °C, 97% R.H.).

### Table 4. Mix design.

| Mix ID | OPC/% | Superplasticizer/% | NaHCO$_3$/% | Na$_2$CO$_3$/% | W/C |
|--------|-------|--------------------|-------------|----------------|-----|
| 1      | 100   | 0.5                | 0           | 0              | 0.35|
| 2      | 1     | 1                  | -           | -              | 1   |
| 3      | 2     | -                  | 4           | -              | 1   |
| 4      | 3     | -                  | -           | 1              | 1   |
| 5      | 100   | 0.5                | 4           | -              | 0.35|
| 6      | -     | 2                  | -           | 2              | 1   |
| 7      | -     | 3                  | -           | 3              | 1   |
| 8      | -     | 4                  | -           | 4              | 1   |

The setting time of cement paste were tested according to a Chinese standard JC477-2005 [32]. A multichannel microcalorimeter was used for hydration heat test and it lasted for 24 h. Cubic samples with a dimension of 40 mm × 40 mm × 40 mm were used for compressive strength test. Compressive strength, TG-DTA, and SEM tests were conducted at ages of 1, 7, and 28 days. Powder samples were collected and the hydration was terminated by immersing into absolute ethyl alcohol for 24 h. The powder samples were then dried at 40 °C in a vacuum oven for 4 h. The samples were furtherly grounded by a pestle and mortar to pass a sieve with an aperture of 75 µm. The final powder samples were used for TG-DTA and XRD tests. The TG-DTA tests were conducted in a N$_2$ environment with a simultaneous thermal analyzer system (HENVEN, Beijing, China) and the temperature was increased from 20 °C to 800 °C at a rate of 10 °C/min. Each time, one gram of the powder sample was used for XRD test. The XRD tests were conducted using a Rigaku SmartLab X-ray diffractometer (Rigaku, Tokyo, Japan) under a voltage of 40 kV and a current of 150 mA. The scanning rate was 10°/min from 5° to 70°. A MERLIN Compactfield Emission Scanning Electron Microscope (ZEISS, Jena, Germany) was used for SEM observations. The selected samples for SEM observations were at a size of around 5 mm in length and width with a fresh broken surface after the compression tests at ages of 1, 7, and 28 days. The samples were gold coated under vacuum condition before observation. The detailed procedures of hydration heat, compressive strength, TG-DTA, XRD, and SEM can also be found in our previous paper [33].

### 3. Results

#### 3.1. Influence of NaHCO$_3$/Na$_2$CO$_3$ on the Setting Time of OPC Paste

The influence of 0%, 1%, 2%, 3%, and 4% of NaHCO$_3$/Na$_2$CO$_3$ on the initial and final setting time of OPC paste is shown in Figure 1. The results show that both of the initial and final setting time of the OPC paste decreased with the increase of NaHCO$_3$ or Na$_2$CO$_3$ content. The initial setting time of OPC paste with 1%, 2%, 3%, and 4% NaHCO$_3$ decreased by 86.76%, 94.12%, 96.69%, and 97.43% respectively compared to that of pure OPC paste. The final setting time of OPC paste with 1%, 2%, 3%, and 4% NaHCO$_3$ decreased by 43.51%, 68.70%, 85.50%, and 86.01% respectively compared to that of pure OPC paste. It can be seen that the addition of 1–2% NaHCO$_3$ significantly decreased the initial and final setting time of OPC paste. Further increase of NaHCO$_3$ beyond 1% up to 4% showed little influence on the initial setting time, and further increase of NaHCO$_3$ beyond 2% up to 4% showed little influence on the final setting time.

The initial setting time of OPC paste with 1%, 2%, 3%, and 4% Na$_2$CO$_3$ decreased by 90.44%, 90.80%, 91.18%, and 91.91% respectively compared to that of pure OPC paste. The final setting time...
of OPC paste with 1%, 2%, 3%, and 4% Na$_2$CO$_3$ decreased by 39.95%, 53.69%, 54.96%, and 64.38% respectively compared to that of pure OPC paste. It can be seen that the influence of Na$_2$CO$_3$ on the initial setting time was more significant than the final setting time. The Na$_2$CO$_3$ showed similar effect as NaHCO$_3$ on the initial setting time but its influence on the final setting time was less than the NaHCO$_3$. The related mechanisms will be discussed later.

![Figure 1](https://via.placeholder.com/150)

**Figure 1.** Effects of NaHCO$_3$ and Na$_2$CO$_3$ on the setting time of OPC paste.

### 3.2. Influence of NaHCO$_3$/Na$_2$CO$_3$ on the Compressive Strength of OPC Paste

The effect of 0%, 1%, 2%, 3%, and 4% of NaHCO$_3$ and Na$_2$CO$_3$ on the compressive strength of OPC paste specimen at the ages of 1, 7, and 28 days is shown in Figure 2. At the age of 1 day, with the increasing content of NaHCO$_3$, the compressive strength of OPC paste increased initially and then decreased. The highest compressive strength happened in the mix with 3% NaHCO$_3$. The strength of the mix with 3% NaHCO$_3$ at the age of 1 day was 14% higher than that of the paste with no NaHCO$_3$. At the age of 7 days, with the increase of NaHCO$_3$, the compressive strength of OPC paste increased initially and then decreased with the highest strength happened in the mix with 1% NaHCO$_3$. The strength of the mix with 1% NaHCO$_3$ at the age of 7 days was 6% higher than that of OPC. At 28 days, the compressive strength of cement paste deceased continuously with the increase of NaHCO$_3$. It can be seen that below 1% NaHCO$_3$ can increase the early age strength but higher content of could decrease the later age strength significantly. This can be caused by the formation of NaOH [20], which is a strong alkali and could react with the silica sand in the paste specimen.

For the pastes with Na$_2$CO$_3$, the compressive strength at ages of 1 and 7 days firstly increased and then decreased with the increase of Na$_2$CO$_3$ content, and the paste with 1% Na$_2$CO$_3$ had the highest compressive strength. The compressive strength of paste with 1% Na$_2$CO$_3$ was 7.2% higher at age of 1 day and 7.7% higher at age of 7 days compared to that of OPC paste. Similarly to NaHCO$_3$, the compressive strength of pastes with Na$_2$CO$_3$ at age of 28 days decreased continuously with the increase of Na$_2$CO$_3$. The reason could be that the formation of NaOH caused the decrease of compressive strength. From Figure 2 it can be seen that the NaHCO$_3$ had the similar beneficial effect as Na$_2$CO$_3$ on the early age strength when the addition was below 1%, but much worse effect than Na$_2$CO$_3$ on the strength development when the addition was above 1%.
3.3. Hydration Heat

Figure 3 shows the hydration heat rate and accumulated hydration heat of the OPC pastes with 0%, 1%, 2%, 3%, and 4% NaHCO₃. The first peak of hydration heat rate at around 0.05 h in Figure 3(a1) firstly decreased with the increase of NaHCO₃ up to 2% and then increased with the further increase of NaHCO₃ up to 4%. The first peak associated with the formation ettringite (AFt) [34,35], and it is suggested that the addition of 1–2% NaHCO₃ refrained the formation of AFt in OPC paste but the further addition of NaHCO₃ up to 4% accelerated the formation of AFt. The initial decrease of the AFt could be caused by the possible reaction or adhesion between the NaHCO₃ and the aluminum phases, but the later increase of the AFt in the mix with 4% NaHCO₃ could be caused by the increased CO₃²⁻ content [17].

Different from the trend of the first peak of hydration heat rate with content of NaHCO₃, as shown in Figure 3(a2), the peak height of the second peak of the hydration heat rate at 8–15 h increased continuously with the increase of NaHCO₃. The second peak associated with the hydration of C₃S and C₂S and the formation of C-S-H and portlandite. It can be seen that the addition of increased the peak of C₃S and C₂S at 8–15 h in the mix with more NaHCO₃. However, the peak time of the second peak was delayed in the mixes with 1% and 2% NaHCO₃ but it was earlier in the mixes with 3% and 4% NaHCO₃ compared to the control group with no NaHCO₃. It suggested that the addition of NaHCO₃ up to 2% delayed the hydration of C₃S and C₂S but further increase of NaHCO₃ up to 4% accelerated the hydration of C₃S and C₂S in the initial 24 h.

The total accumulated hydration heat in the initial 24 h is shown in Figure 3b, and it shows that the difference between the total hydration heat of OPC paste and that of the mix with 1% NaHCO₃ was not significant, the mix with 2% had a much lower hydration heat than the OPC paste, but the mixes with 3% and 4% had a significantly higher total hydration heat than the OPC paste. This was mainly caused by the previously described delayed effect on the hydration heat in the mix with 2% NaHCO₃ and the accelerated effect on the hydration heat in the mixes with 3% and 4% NaHCO₃.
Figure 3. Cont.
There was a tendency that the total hydration heat of the mixes with 3% and 4% Na$_2$CO$_3$ could be lower than the control group in the long term.

This suggested that, in the mixes with Na$_2$CO$_3$, the initial accelerated formation of AFt in the first peak might consumed most of the C$_3$A and formation of most AFt was finished at that time.

As for the second peak, in Figure 4(a2), the addition of Na$_2$CO$_3$ increased the peak height and accelerated the peak time compared to the OPC paste with no Na$_2$CO$_3$. It suggested that the Na$_2$CO$_3$ accelerated and increased the hydration of C$_3$S and C$_2$S. This agrees with the findings in literature [33]. There was a shoulder peak at around 18 h after the second peak in the control group, which was caused by the secondary formation of AFt [36], but this shoulder peak did not appear in any mix with Na$_2$CO$_3$. This suggested that, in the mixes with Na$_2$CO$_3$, the initial accelerated formation of AFt in the first peak might consumed most of the C$_3$A and formation of most AFt was finished at that time.

The accumulated hydration heat of the mixes with different contents of Na$_2$CO$_3$ is shown in Figure 4b. It can be seen that the mix with Na$_2$CO$_3$ had a much higher accumulated hydration heat compared to the control group. At 5–10 h, the mix with 4% Na$_2$CO$_3$ had the highest accumulated hydration heat and the higher content of Na$_2$CO$_3$ caused a higher accumulated hydration heat. At the end of 24 h, the mix with 1% Na$_2$CO$_3$ had the highest total hydration heat, followed by the mixes with 3%, 2%, 4%, and 0% Na$_2$CO$_3$. After 15 h, the increase rate of the accumulated hydration heat in the mixes with 3% and 4% Na$_2$CO$_3$ decreased obviously compared to the mixes with 1% and 2% Na$_2$CO$_3$. There was a tendency that the total hydration heat of the mixes with 3% and 4% Na$_2$CO$_3$ could be lower than the control group in the long term.

Figure 3. Hydration heat rate (a) and accumulated heat (b) of the pastes with different contents of NaHCO$_3$. 

The hydration heat rate and accumulated hydration heat of the mixes with 0%, 1%, 2%, 3%, and 4% Na$_2$CO$_3$ are shown in Figure 4. The results show that the mixes with Na$_2$CO$_3$ had a higher first peak height of the hydration heat rate, as in Figure 4(a1), than the OPC paste with no Na$_2$CO$_3$. The highest first peak height happened in the mix with 3% Na$_2$CO$_3$ and there was a slightly decrease of the peak height in the mix with 4% Na$_2$CO$_3$. It is indicated that the addition of Na$_2$CO$_3$ accelerated the hydration of C$_3$A and the formation of AFt. 

As for the second peak, in Figure 4(a2), the addition of Na$_2$CO$_3$ increased the peak height and accelerated the peak time compared to the OPC paste with no Na$_2$CO$_3$. The highest first peak height happened in the mix with 3% Na$_2$CO$_3$ and there was a slightly decrease of the peak height in the mix with 4% Na$_2$CO$_3$. It is indicated that the addition of Na$_2$CO$_3$ accelerated the hydration of C$_3$A and the formation of AFt.

Figure 4. Hydration heat rate (a) and accumulated heat (b) of the pastes with different contents of Na$_2$CO$_3$. The accumulated hydration heat of the pastes with different contents of Na$_2$CO$_3$ is shown in Figure 4b. It can be seen that the mix with Na$_2$CO$_3$ had a much higher accumulated hydration heat compared to the control group. At 5–10 h, the mix with 4% Na$_2$CO$_3$ had the highest accumulated hydration heat and the higher content of Na$_2$CO$_3$ caused a higher accumulated hydration heat. At the end of 24 h, the mix with 1% Na$_2$CO$_3$ had the highest total hydration heat, followed by the mixes with 3%, 2%, 4%, and 0% Na$_2$CO$_3$. After 15 h, the increase rate of the accumulated hydration heat in the mixes with 3% and 4% Na$_2$CO$_3$ decreased obviously compared to the mixes with 1% and 2% Na$_2$CO$_3$. There was a tendency that the total hydration heat of the mixes with 3% and 4% Na$_2$CO$_3$ could be lower than the control group in the long term.
Figure 4. Cont.
There were three main DTA peaks at around 100 °C, 460 °C, and 700°C, which indicated the composition of AFt, portlandite and CaCO$_3$ respectively. At the age of 1 day, the weight loss at the peak of AFt was 2.6%, 2.9%, 2.7%, 2.6%, and 3.1% in the mix with 0%, 1%, 2%, 3%, and 4% NaHCO$_3$ respectively. The weight loss at the peak of portlandite was 2.0%, 1.6%, 1.5%, 1.2%, and 1.0% in the mix with 0%, 1%, 2%, 3%, and 4% NaHCO$_3$ respectively. The weight loss at the peak of CaCO$_3$ was 3.5%, 3.9%, 4.0%, 4.8%, and 4.7% in the mix with 0%, 1%, 2%, 3%, and 4% NaHCO$_3$ respectively. It can be seen that, similar as the NaHCO$_3$, the addition of NaHCO$_3$ increased the formation of AFt and CaCO$_3$ at the age of 1 day but decreased the portlandite. At the age of 7 and 28 days, the weight losses at the peaks of AFt, portlandite and CaCO$_3$ showed similar trend as that at age of 1 day. It can be seen that the addition of NaHCO$_3$ increased the formation of AFt and CaCO$_3$ and decreased the portlandite at all the ages.

Figure 6 shows the TG-DTA results of the mixes with 0%, 1%, 2%, 3%, and 4% NaHCO$_3$ at the ages of 1, 7, and 28 days. At the age of 1 day, the weight loss at the peak of AFt was 2.6%, 2.6%, 3.0%, 2.8%, and 3.0% in the mix with 0%, 1%, 2%, 3%, and 4% NaHCO$_3$ respectively. The weight loss at the peak of portlandite was 2.0%, 1.6%, 1.4%, 1.1%, and 0.9% in the mix with 0%, 1%, 2%, 3%, and 4% Na$_2$CO$_3$ respectively. The weight loss at the peak of CaCO$_3$ was 3.5%, 3.9%, 4.0%, 4.8%, and 4.7% in the mix with 0%, 1%, 2%, 3%, and 4% Na$_2$CO$_3$ respectively. It can be seen that, similar as the NaHCO$_3$, the addition of Na$_2$CO$_3$ increased the formation of AFt and CaCO$_3$ and decreased the portlandite at the age of 1 day. This trend was similar at the ages of 7 and 28 days.

These results showed that the influence of NaHCO$_3$ on the formation of AFt, portlandite and CaCO$_3$ was similar as Na$_2$CO$_3$. The mix with the highest amount of NaHCO$_3$ or Na$_2$CO$_3$ had the highest amount of AFt and CaCO$_3$ but the lowest amount of portlandite. As can be seen from Figures 5 and 6, the addition of NaHCO$_3$ or Na$_2$CO$_3$ made the overall weight loss of the blended paste higher than the control group at the age of 1 and 7 days but the lower than the control group at the age of 28 days.
Figure 5. TG-DTA results of the pastes with different contents of NaHCO₃ at ages of (a) 1, (b) 7, and (c) 28 days.
Figure 6. TG-DTA results of the pastes with different contents of Na$_2$CO$_3$ at ages of (a) 1, (b) 7, and (c) 28 days.
3.5. XRD Results

The XRD results of the pastes with 0%, 1%, 2%, 3%, and 4% NaHCO$_3$ at the ages of 1, 7, and 28 days are shown in Figure 7. It can be seen that, at the age of 1 day, the peaks of Ca(OH)$_2$ at $2\theta = 34^\circ$ and $47^\circ$ decreased with the increase of NaHCO$_3$. At the ages of 7 and 28 days, the peaks of portlandite changed in the same way as that in 1 day, besides, the peak of C-S-H and CaCO$_3$ at $2\theta = 29^\circ$ increased with the increase of NaHCO$_3$. These results all agree with the previously reported findings in the TG-DTA results. The change of AFt in the XRD spectrum was not obvious for the mixes with different contents of NaHCO$_3$.

Figure 8 shows the XRD results of the pastes with 0%, 1%, 2%, 3%, and 4% Na$_2$CO$_3$ at the ages of 1, 7, and 28 days. The results show that the peaks of C-S-H and CaCO$_3$ increased with the increase of Na$_2$CO$_3$ content at all ages, at the same time, the portlandite decreased gradually with the increase of Na$_2$CO$_3$ content. This again agrees with the findings in TG-DTA results.

Figure 7. Cont.
Figure 7. XRD spectrum results of the mixes with different contents of NaHCO₃ at ages of (a) 1, (b) 7, and (c) 28 days.

Figure 8. Cont.
with the results of XRD and compressive strength. It could be indicated that the early age strength at 1 day was mainly influenced by both ettringite and C-S-H gel, and the later age strength, such as 28 days, was mainly influenced by C-S-H gel structure.

3.6. SEM Results

The SEM results of the pastes with 0%, 1%, 2%, 3%, and 4% NaHCO₃ at the ages of 1, 7, and 28 days are shown in Figure 9. At the age of 1 day, it can be seen that the amount of needle-shaped ettringite in the mix with NaHCO₃ was higher than that in the pure OPC paste. The microstructure of the C-S-H gel in the mixes with 1%, 2%, and 3% was denser than that in the pure OPC paste, but the C-S-H gel in the mix with 4% was a bit loose compared to the other groups. These agrees with the changing trend of the compressive strength with NaHCO₃ at 1 day in Figure 2. At the age of 7 days, the mix with 1% NaHCO₃ had more ettringite and denser C-S-H gel than the pure OPC paste, but the C-S-H gel in the mixes with NaHCO₃ was looser than that in pure OPC paste. These agree with the results of XRD and compressive strength.

Figure 10 shows the SEM images of the mixes with 0%, 1%, 2%, 3%, and 4% NaHCO₃ at the ages of 1, 7, and 28 days. At the age of 1 and 7 days, the mix with 1% NaHCO₃ had more ettringite and a denser C-S-H structure than the pure OPC paste. The mixes with 2–4% had more ettringite but a worse C-S-H gel structure than the pure OPC paste. At the age of 28 days, the C-S-H gel became worse with the increase of Na₂CO₃ content compared to the OPC paste with no Na₂CO₃. These results agree with the compressive strength results as shown in Figure 2. It could be indicated that the early age strength at 1 day was mainly influenced by both ettringite and C-S-H gel, and the later age strength, such as 28 days, was mainly influenced by C-S-H gel structure.

Figure 8. XRD spectrum results of the mixes with different contents of Na₂CO₃ at ages of (a) 1, (b) 7, and (c) 28 days.
Figure 9. SEM results of the mixes with different contents of NaHCO₃ at ages of (a) 1, (b) 7, and (c) 28 days.
Figure 10. (a) 1 day

(b) 7 days

Figure 10. Cont.
4. Discussion

4.1. Influence of Na$_2$CO$_3$/NaHCO$_3$ on the PH of OPC Paste

It is known that both Na$_2$CO$_3$ and NaHCO$_3$ are soluble and their main difference is that Na$_2$CO$_3$ dissolves into Na$^+$ and CO$_3^{2-}$ and the NaHCO$_3$ dissolves into Na$^+$ and HCO$_3^-$ in water as shown in Equations (1) and (2). Solutions of Na$_2$CO$_3$ or NaHCO$_3$ have a PH > 7, and the PH of Na$_2$CO$_3$ solution is higher than that of bicarbonate solution when the same content of the two are added. For example, under the same concentration 1 mmol/L (25 °C and 1 atm), the PH values of Na$_2$CO$_3$ and NaHCO$_3$ solutions are 10.52 and 8.27 respectively. When they are added in cement paste, both of them can react with the portlandite, which is a hydration product of cement, and form CaCO$_3$, as Equations (3) and (4). Cement slurry was prepared for pH measurements with a water-cement ratio of 0.5, a water reducing agent of 0.5%, and Na$_2$CO$_3$ and NaHCO$_3$ of 0%, 1%, 2%, 3%, and 4%. The pH meter was initially calibrated with a neutral solution (pH = 7) and then with an alkaline solution with a known pH. After the calibration is completed, the electrode of the pH meter was immersed into the cement slurry and the slurry was gently vibrated to reach a uniform state during the measurements. The pH value was recorded after the reading was stable. The measured pH results are shown in Figure 11. It can be seen the pH of the OPC paste increased with the increase of Na$_2$CO$_3$ but it decreased with the increase of NaHCO$_3$. This was caused by the different pH of the solutions with the same amount of Na$_2$CO$_3$ and NaHCO$_3$. There could be a risk of alkali silica reaction in the concrete with a high amount of Na$_2$CO$_3$ because of the increased pH. There could be a decay of the C-S-H gel in the concrete with a high amount of NaHCO$_3$ because of the decreased pH.

\[
\text{Na}_2\text{CO}_3 \rightarrow 2\text{Na}^+ + \text{CO}_3^{2-} \quad (1)
\]
\[
\text{NaHCO}_3 \rightarrow \text{Na}^+ + \text{HCO}_3^- \quad (2)
\]
\[
\text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 = \text{CaCO}_3 \downarrow + 2\text{NaOH} \quad (3)
\]
\[
\text{NaHCO}_3 + \text{Ca(OH)}_2 = \text{NaOH} + \text{CaCO}_3 \downarrow + \text{H}_2\text{O} \quad (4)
\]
While in the paste with NaHCO₃, the initial reactions were as Equations (4), (5), and (7), and there was formation of both CaCO₃ and ettringite. While in the paste with Na₂CO₃, the initial reactions were as Equations (3) and (5)–(7), and there was formation of both CaCO₃ and ettringite. The difference of Na⁺ reactions were as Equations (3) and (5)–(7), and there was formation of both CaCO₃ and ettringite. In Na₂CO₃, the weight of Na⁺ is 43.4% and the weight of CO₂ is 41.5%. In NaHCO₃, the weight of Na⁺ is 27.4% and the weight of CO₂ is 52.4%. It can be seen that, when the same weight of the two are used, NaHCO₃ brings 16% less Na⁺ and 10.9% more CO₂ into the cement paste. Although the Na⁺ is believed to accelerate the initial hydration and early age strength [37], it is thought that Na⁺ is responsible for the adverse effect on the later age strength development of the cement paste with salts containing Na⁺ [20]. The adverse effect of Na⁺ on the strength development can be explained that the Na⁺ could affect the adhesion between C-S-H gel structure (Figure 12a) by reaction with the silica phase in the cement paste and form sodium orthosilicate (Figure 12b) [38,39]. The difference of Na⁺ introduced by the two was thought to be the main reason that the paste with NaHCO₃ had a better later stage strength development than that with Na₂CO₃.

![Graph](image.png)

**Figure 11.** pH of fresh cement paste with Na₂CO₃ or NaHCO₃.

### 4.2. Influence of Na₂CO₃/NaHCO₃ on the Introduced CO₂

In Na₂CO₃, the weight of Na⁺ is 43.4% and the weight of CO₂ is 41.5%. In NaHCO₃, the weight of Na⁺ is 27.4% and the weight of CO₂ is 52.4%. It can be seen that, when the same weight of the two are used, NaHCO₃ brings 16% less Na⁺ and 10.9% more CO₂ into the cement paste. Although the Na⁺ is believed to accelerate the initial hydration and early age strength [37], it is thought that Na⁺ is responsible for the adverse effect on the later age strength development of the cement paste with salts containing Na⁺ [20]. The adverse effect of Na⁺ on the strength development can be explained that the Na⁺ could affect the adhesion between C-S-H gel structure (Figure 12a) by reaction with the silica phase in the cement paste and form sodium orthosilicate (Figure 12b) [38,39]. The difference of Na⁺ introduced by the two was thought to be the main reason that the paste with NaHCO₃ had a better later stage strength development than that with Na₂CO₃.

![Image](image.png)

**Figure 12.** Sketch of the structure of C-S-H gel (a) and sodium orthosilicate (b).

### 4.3. Influence of Na₂CO₃/NaHCO₃ on the Formation of Ettringite and CaCO₃

The initial difference between the effects of the Na₂CO₃ and NaHCO₃ on the setting time and early age strength can be explained by the following reasons. In the paste with Na₂CO₃, the initial reactions were as Equations (3) and (5)–(7), and there was formation of both CaCO₃ and ettringite. While in the paste with NaHCO₃, the initial reactions were as Equations (4), (5), and (7), and there was formation of both CaCO₃ and ettringite.
no initial formation of CaCO$_3$ and there was only formation of ettringite. There could be less ettringite formed in the paste with Na$_2$CO$_3$ compared to that with NaHCO$_3$ because of the initial consumption of Ca$^{2+}$ with CO$_3^{2−}$. This could contribute to the better initial performance and shorter setting time of the paste with NaHCO$_3$. In the paste with NaHCO$_3$ the formation of CaCO$_3$ happened at a later stage as Equations (8) and (9), and the later stage formed CaCO$_3$ particles could contribute to fill the micro- and nano-pores of the C-S-H gel.

\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2−} + 2\text{H}_2\text{O}
\]

(5)

\[
\text{CO}_3^{2−} + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 \downarrow
\]

(6)

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + 26\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}
\]

(7)

\[
\text{C}_3\text{S} + \text{H}_2\text{O} \rightarrow \text{C-S-H} + \text{Ca}^{2+} + \text{OH}^{−}
\]

(8)

\[
\text{HCO}_3^{−} + \text{Ca}^{2+} + \text{OH}^{−} \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}
\]

(9)

4.4. Influence of Na$_2$CO$_3$/NaHCO$_3$ on the Enthalpies of the Reactions with C$_3$S

In order to further investigate the effect of Na$_2$CO$_3$ and NaHCO$_3$ on the hydration of C$_3$S, the enthalpies of the reactions are calculated. The enthalpies of all the reactants and products were calculated by the first-principles and the module of total energy pseudopotential calculations in the Vienna Ab initio Simulation Package (VASP) [40] was used for the calculations.

\[
2(3\text{CaO} \cdot \text{SiO}_2) + 6\text{H}_2\text{O} = 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{Ca(OH)}_2
\]

(10)

\[
\text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{NaOH}
\]

(11)

\[
\text{Ca(OH)}_2 + \text{NaHCO}_3 = \text{CaCO}_3 + \text{NaOH} + \text{H}_2\text{O}
\]

(12)

\[
3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 2\text{NaOH} = \text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O} + \text{Ca(OH)}_2 + \text{H}_2\text{O}
\]

(13)

By combing Equations (10), (11) and (13), resulting Equation (14)

\[
2(3\text{CaO} \cdot \text{SiO}_2) + \text{Na}_2\text{CO}_3 + 4\text{H}_2\text{O} = \text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O} + \text{CaCO}_3 + 3\text{Ca(OH)}_2
\]

(14)

By combing Equations (10), (12) and (13), resulting Equation (15)

\[
2(3\text{CaO} \cdot \text{SiO}_2) + 2\text{NaHCO}_3 + 2\text{H}_2\text{O} = \text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O} + 2\text{CaCO}_3 + 2\text{Ca(OH)}_2
\]

(15)

The enthalpy of the reactions in Equation (14) ($E_{\text{reaction14}}$) can be calculated by Equation (16) and the value was $−0.02903 \text{ eV/atom}$. The enthalpy of the reactions in Equation (15) ($E_{\text{reaction15}}$) can be calculated by Equation (17) and the value was $−0.04306 \text{ eV/atom}$. These negative values suggest that the reactions in Equations (14) and (15) are both exothermic and can proceed spontaneously in thermodynamics. The reaction in Equation (15) had a more negative value than that in Equation (14) and it means that the reaction in Equation (15) is much easier to happen than that in Equation (14), which suggests that the reaction between C$_3$S and NaHCO$_3$ is much easier that the reaction between C$_3$S and Na$_2$CO$_3$.

\[
E_{\text{reaction14}} = (E_{\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O} \times 16 + E_{\text{CaCO}_3} \times 5 + E_{\text{Ca(OH)}_2} \times 15 - E_{3\text{CaO} \cdot \text{SiO}_2} \times 18 - E_{\text{Na}_2\text{CO}_3} \times 6 - E_{\text{H}_2\text{O}} \times 12)/36
\]

(16)

\[
E_{\text{reaction15}} = (E_{\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O} \times 16 + E_{\text{CaCO}_3} \times 10 + E_{\text{Ca(OH)}_2} \times 10 - E_{3\text{CaO} \cdot \text{SiO}_2} \times 18 - E_{\text{NaHCO}_3} \times 18 - E_{\text{H}_2\text{O}} \times 6)/36
\]

(17)
5. Conclusions

The influence of NaHCO$_3$ and Na$_2$CO$_3$ as additional additives on the setting time and compressive strength of OPC paste was investigated and the related effect on the hydration mechanism was studied through TG-DTA, XRD, and SEM tests. The following conclusions can be drawn.

(1) The initial and final setting time of OPC paste decreased with the increase of either NaHCO$_3$ or Na$_2$CO$_3$.

(2) The addition of either NaHCO$_3$ or Na$_2$CO$_3$ could increase the early age compressive strength (1 and 7 days) depending on the content added but they could decrease the compressive strength at later ages, such as 28 days, with the increase of content added.

(3) As an accelerator, the optimum content of NaHCO$_3$ and Na$_2$CO$_3$ were found to be in the same level as 1% of the weight of OPC. The addition 1% of either of the two accelerators could significantly shorten the setting time, increase the early age strength and did not have an obvious detrimental effect on the later age strength.

(4) Further increase of NaHCO$_3$ and Na$_2$CO$_3$ above 1% could decrease the compressive strength of OPC paste although the ettringite formation was accelerated and increased. This decay was mainly caused by the Na$^+$ ions introduced and the Na$^+$ could partly replace the Ca$^{2+}$ in the C-S-H gel and cause the discontinuity of the C-S-H gel.

(5) NaHCO$_3$ was seen to be a better option as an accelerator compared to Na$_2$CO$_3$. The reaction between NaHCO$_3$ and C$_3$S was found to be much easier than the reaction between Na$_2$CO$_3$ and C$_3$S. The same amount addition of NaHCO$_3$ resulted a higher compressive strength at all ages compared to NaHCO$_3$. Besides, NaHCO$_3$ the introduced less Na$^+$ and more CO$_2$ in the cementitious system than the Na$_2$CO$_3$ when the same amount of the two were used.

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