



The influence of sodium hydrogen carbonate on the hydration of cement



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HIGHLIGHTS

- The effect of addition of NaHCO_3 on cement paste and mortar was investigated.
- Adding NaHCO_3 resulted in the consumption of Ca(OH)_2 and the production of CaCO_3 .
- High alkalinity of cement paste was maintained by adding NaHCO_3 .
- Test results provide a new insight into potential means to improve the durability.

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ABSTRACT

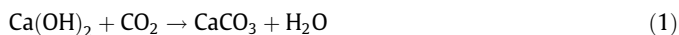
The presence of Ca(OH)_2 may adversely influence resistance to sulfates, while its absence reduces the pH, leading to corrosion of the steel in reinforced concrete. Test results of the present study showed that adding NaHCO_3 allowed carbonation to occur uniformly within the cement paste, resulting in the consumption of Ca(OH)_2 . Despite the consumption of Ca(OH)_2 , the pH was found to increase by production of NaOH . Strength test results showed that an addition of NaHCO_3 of less than 5% enhanced the strength, but that exceeding 5% had an adverse effect. The results here provide new insight into potential means to improve the durability of concrete.

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1. Introduction

Portland cement, the most widely used construction material in the world, produces calcium silicate hydrates (C-S-H), calcium hydroxide (Ca(OH)_2), and AFm (Al_2O_3 - Fe_2O_3 -mono) phases through a hydration reaction. Hardened cement paste mostly consists of the C-S-H phase, and its pore solution retains a pH value of approximately 13 due to the presence of calcium hydroxide and alkali metal ions [1]. Reinforced concrete, which is composed of cement paste, aggregates and steel reinforcement, is known to be a highly durable material, though numerous cases of deterioration under various exposure conditions were reported from the middle of the twentieth century. Among the cement hydration products, which can potentially provide a medium for deterioration reactions, the effect of calcium hydroxide on the deterioration of hardened concrete is obvious. For instance, calcium hydroxide reacts with carbon dioxide in the atmosphere through the reaction of

Eq. (1), producing calcium carbonate, whose pore solution reduces pH and is ultimately responsible for the corrosion of steel [2]



In addition, calcium hydroxide can react with sulfate and decompose into gypsum, as expressed in Eq. (2), inducing cracks due to the expansion of the concrete [3]

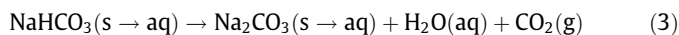


Therefore, it can be concluded that the presence of calcium hydroxide can adversely influence the sulfate resistance of concrete whereas its absence reduces the pH, inducing steel corrosion.

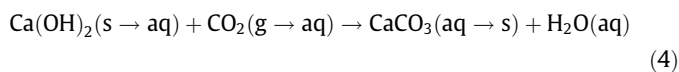
Sodium hydrogen carbonate, also known as sodium bicarbonate or baking soda, exhibits low acidity when dissolved in water. While the powder decomposes at 270 °C, decomposition slowly occurs even at room temperature and the rate dramatically increases above 50 °C [4]. Since the hydration reaction of cement is exothermic and accompanies a rise in the temperature, sodium hydrogen carbonate can be adequately decomposed within cement paste. The decomposition reaction of sodium hydrogen carbonate is given in Eq. (3) [8]. It produces gaseous carbon dioxide

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The emitted carbon dioxide can react with calcium hydroxide, leading to a carbonation reaction which produces calcium carbonate, as provided in Eq. (4) [6]



As a result, it is possible that the series of reactions can uniformly carbonate calcium hydroxide within the cement paste; however, the effect of sodium hydrogen carbonate on the change of the hydration products and on the pH in cement paste remains unclear thus far. Therefore, the aim of the present study is to investigate the effect of an addition of sodium hydrogen carbonate on the characteristics of cement paste and mortar in terms of reaction products, pH and mechanical strength.

2. Material and methods

Conventional Portland cement with a specific gravity of 3.2 produced by Ssangyong Cement Industrial Co., Ltd. was used in this study. Sodium hydrogen carbonate (NaHCO_3) with a purity level of 99.5%, produced by Junsei Chemical Co., Ltd., was added to the cement at the levels of 0, 1, 2, 5 and 10% by the weight of the cement. The water, cement and sand used to fabricate a mortar specimen were mixed at a constant ratio of 1:2:5. The specimens were cast as follows: the dry-mixing of cement, sand and NaHCO_3 was conducted for three minutes to ensure uniformity in the dry mix, after which water was added to the mixture, which was then mixed for a further five minutes. The mortar was cast into a $40 \times 40 \times 160$ mm mold. The specimens were demolded after 24 h and cured in water at 20°C until the day of testing.

The effect of NaHCO_3 on the change of the hydration products in the cement paste was investigated by means of a thermogravimetry/differential thermal analysis (TG/DTA). The pH of the pore solution was measured using a powder suspension made with crushed mortar. 5 g of a uniformly crushed specimen and 25 ml of distilled water were stirred in a stirrer at 150 rpm for 15 min. The suspension was then left stationary for 10 min before measuring the pH. The flexural strength test was conducted in accordance with ASTM C348, using two prism specimens for each batch. The compressive strength was measured using portions of the prisms broken in flexure, in accordance with ASTM C349. Three specimens per batch with a cross-sectional area of 40×40 mm were tested. A universal testing machine was used for both strength tests.

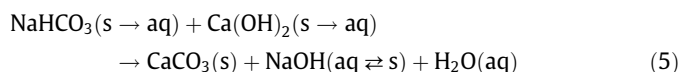
3. Results and discussion

The TG/DTA results for samples aged for 28 days with different amount of NaHCO_3 added are shown in Fig. 1. The DTA curve in Fig. 1 shows the occurrence of endothermic reactions around 450°C and 720°C , indicating the presence of $\text{Ca}(\text{OH})_2$ and CaCO_3 , respectively. The contents of the $\text{Ca}(\text{OH})_2$ and CaCO_3 in each sample were calculated by determining the weight loss in the region where an endothermic reaction occurred, as presented in Fig. 1. The result clearly suggests that the addition of NaHCO_3 resulted in the consumption of $\text{Ca}(\text{OH})_2$ and the production of CaCO_3 . The reduction in the $\text{Ca}(\text{OH})_2$ content became more evident as the amount of added NaHCO_3 increased. In particular, the amount of $\text{Ca}(\text{OH})_2$ consumption and CaCO_3 production underwent a dramatic change when the NaHCO_3 addition exceeded 5%. When 5% and 10% of NaHCO_3 were added, the amounts of $\text{Ca}(\text{OH})_2$ were reduced by 5.8% and 3.0%, respectively. It should be noted that the remaining content of $\text{Ca}(\text{OH})_2$ is similar to the result obtained when using high-volume fly ash cement paste, where the

remaining amount of $\text{Ca}(\text{OH})_2$ is reported to be less than 5% due to a pozzolanic reaction [5].

The measured pH values of samples with different amount of added NaHCO_3 are listed in Table 1. The pH values of the samples aged until 14 days were found to be approximately 12.4 regardless of the amount of NaHCO_3 added. From that point onward, samples with 0% and 1% addition of NaHCO_3 experienced a gradual decrease in their pH levels, showing pHs as low as 11.928 and 11.950, respectively at 56 days of age. It is certain that natural carbonation contributed to a reduction in the amount of $\text{Ca}(\text{OH})_2$ and to the pH level [6]. On the other hand, samples with higher amounts of NaHCO_3 added tended to have a high pH, as evident from samples with NaHCO_3 additions of more than 2%, which retained a pH of more than 12 even after 56 days.

The behavior of the hydration products and pH variations presented in Fig. 1 and in Table 1 present an interesting fact. Natural carbonation, the addition of NaHCO_3 and an addition of pozzolan all lead to $\text{Ca}(\text{OH})_2$ consumption, but the resultant pH change differs in all cases. In general, natural carbonation causes the consumption of $\text{Ca}(\text{OH})_2$ which is dissolved in a pore solution and the production of CaCO_3 , leading to a decrease in the pH [6]. Similarly, a pozzolanic reaction consumes $\text{Ca}(\text{OH})_2$ and produces additional C-S-H and C-A-H during the hydration process, leading to a decrease in the pH as well [7]. In contrast, uniform internal carbonation as a result of the addition of NaHCO_3 consumes $\text{Ca}(\text{OH})_2$ and produces CaCO_3 , while the pH instead increases. The experimental results from the present study suggest that the reaction mechanism of NaHCO_3 in cement paste is expressed as follows:



Eq. (5) presents the reaction between NaHCO_3 and $\text{Ca}(\text{OH})_2$, which produces CaCO_3 and the additional high-pH product NaOH. The solubility of NaOH is 111 g/100 ml at 20°C , which is significantly higher than that of $\text{Ca}(\text{OH})_2$, which is 0.173 g/100 ml [4]. Therefore, it is concluded that an addition of NaHCO_3 not only carbonates internally and uniformly within cement paste to consume $\text{Ca}(\text{OH})_2$, but also produces NaOH which possesses a high pH and good solubility, consequently allowing the pH of the pore solution to remain high. Furthermore, CaCO_3 , a carbonation product, is more thermodynamically stable and less vulnerable to decomposition in comparison with other hydrates [9]. It may fill the pores and reduce the permeability of hardened cement, influencing the durability. The mechanism by which $\text{Ca}(\text{OH})_2$ is consumed and a high pH maintained in the pore solution can provide new insight into a viable alternative to improve concrete durability by the prevention of steel corrosion and sulfate attack. Further studies are necessary to investigate the long-term behavior of hardened cement composites incorporating NaHCO_3 (e.g., the change in pH, microstructure and durability).

The flexural and compressive strengths of specimens with different NaHCO_3 additions are shown in Fig. 2. It was observed in both strength tests that the addition of NaHCO_3 clearly affects the strength. Samples with NaHCO_3 added at amounts of 1% and 2% experienced an increase in both the compressive and flexural strengths, indicating that adding NaHCO_3 had a positive effect on the development of strength in these materials. Samples with a 5% addition showed delayed strength development at an early age in comparison with that of the control, while the flexural strengths at 56 days age were similar. However, a 10% addition resulted in significantly lower strength compared to the control, suggesting that an excessive addition of NaHCO_3 adversely affect the strength. The optimal amount of added NaHCO_3 is therefore suggested to lie between 2% and 5% so as to allow internal

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