Summary of CO₂ curing concrete technology

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Abstract. In recent years, China has a large amount of infrastructure projects and increasingly serious environmental pollution. The impact of CO₂ and other greenhouse gases on the climate is becoming more and more significant. With the proposal of the national “double carbon” goal and green development strategy, exploring a new model of carbon sequestration has become a research hotspot. This paper comprehensively expounds the technology of carbon dioxide curing concrete, and introduces the mechanism of the technology, the influencing factors in the curing process, and the influence of carbon dioxide curing on concrete. It is found that the water binder ratio of concrete, raw materials such as aggregates, and the concentration, pressure, pre-curing and other external conditions of carbon dioxide have different degrees of influence on the curing of concrete; In addition, it is also found that CO₂ curing improves the mechanical properties, microstructure and durability of concrete. Finally, the research on CO₂ curing concrete technology is summarized and the future development is prospected.

Keywords: Carbon dioxide curing; Concrete; Action mechanism.

1. Introduction

Carbon dioxide curing concrete technology refers to a green, environment-friendly and new curing concrete technology that chemically reacts the carbonatable cement components in fresh concrete, such as tricalcium silicate (C₃S) and dicalcium silicate (C₂S) with CO₂ gas to produce calcium carbonate and silica gel, which provides an effective way for carbon dioxide storage.

It is estimated that the use of CO₂ in concrete building materials can remove, utilize and store 0.1 to 1.4 GT CO₂ yr⁻¹. The storage of CO₂ is far beyond the service life of the infrastructure itself. The absorption of CO₂ by buildings is expected to account for about 4.29% of the carbon emission in the concrete production stage. The increasing role of the concrete industry in reducing carbon dioxide emissions has created a new way for the future demand for concrete and its corresponding raw materials.

Portland cement has good carbon dioxide absorption capacity and working strength characteristics. Its reaction device is as follows:

Fig.1 Carbon dioxide curing device schematic

Carbon dioxide curing concrete technology can not only fix carbon and play a positive role in reducing greenhouse gases, reducing energy consumption and regulating the global climate, but also have a hydration reaction between carbon dioxide and cement components, which can also accelerate the strength development of concrete. Carbon dioxide curing concrete technology makes concrete specimens show good performance in dimensional stability, mechanical properties and durability.
Based on the previous research, this paper comprehensively introduces the action mechanism and influencing factors of carbon dioxide curing concrete technology, as well as the influence of this technology on the macro performance and microstructure of concrete. The purpose is to further improve the carbon fixation efficiency, optimize the performance of concrete and explore a new way of technological development.

2. Action mechanism of carbon dioxide curing technology

CO₂ curing concrete is mainly the hydration reaction between CO₂ and cement clinker minerals such as tricalcium silicate (C₃S), dicalcium silicate (C₂S), tricalcium aluminate (C₃A), tetracalcium ferroaluminate (C₄AF). The reaction process between various components of cement clinker and carbon dioxide in the process of carbon dioxide curing concrete can be expressed by formula (1) and formula (2):

\[
3\text{CaO} \cdot \text{SiO}_2 + 3\text{CO}_2 + y\text{H}_2\text{O} \rightarrow \text{SiO}_2 \cdot y\text{H}_2\text{O} + 3\text{CaCO}_3 \quad (1)
\]

\[
2\text{CaO} \cdot \text{SiO}_2 + 2\text{CO}_2 + y\text{H}_2\text{O} \rightarrow \text{SiO}_2 \cdot y\text{H}_2\text{O} + 2\text{CaCO}_3 \quad (2)
\]

Carbon dioxide curing concrete is a complex process. The state before and during carbon dioxide curing is shown in Figure 2:

![Fig.2 Schematic drawing of cement particle before and during CO₂ curing](image)

3. Influencing factors of carbon dioxide curing concrete

There are many influencing factors of carbon dioxide curing concrete, such as raw materials such as aggregate; Water binder ratio, pre curing, carbon dioxide pressure, carbon dioxide concentration and other preparation conditions and curing environment. It is generally believed that the carbon dioxide curing process of concrete is mainly controlled by the reactivity of raw materials and the diffusion rate of carbon dioxide.

3.1 Water binder ratio

It is found that [7-8], the water binder ratio has a significant impact on the strength, porosity, microstructure, workability and durability of concrete products. The greater the water binder ratio, the greater the porosity in the concrete, so the faster the carbonation rate of the concrete. A higher water cement ratio can enhance the mechanical strength effect of carbon dioxide curing concrete.

Tu Zhenjun, Shi Caijun and others proposed to cure concrete by carbon dioxide mineralization by controlling the residual water binder ratio. It was found that the residual water binder ratio has a great impact on carbon dioxide cured concrete. When the residual water binder ratio is 0.16 ~ 0.20, the carbon dioxide curing degree of concrete is the largest, the compressive strength after curing is also the highest, and the utilization efficiency of CO₂ and the reaction degree of specimens are higher. Especially when the water cement ratio is 0.18, the CO₂ curing degree will reach the peak.
Table 1. results after CO$_2$ curing of specimens with different residual water cement ratio (R-W / C)

<table>
<thead>
<tr>
<th>R-W / C</th>
<th>CO$_2$养护程度/%</th>
<th>抗压强度/MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14</td>
<td>36.18</td>
<td>13.0</td>
</tr>
<tr>
<td>0.16</td>
<td>39.19</td>
<td>14.4</td>
</tr>
<tr>
<td>0.18</td>
<td>40.18</td>
<td>15.1</td>
</tr>
<tr>
<td>0.20</td>
<td>37.46</td>
<td>13.6</td>
</tr>
<tr>
<td>0.22</td>
<td>35.69</td>
<td>12.9</td>
</tr>
<tr>
<td>0.24</td>
<td>34.56</td>
<td>12.6</td>
</tr>
<tr>
<td>0.26</td>
<td>31.21</td>
<td>11.5</td>
</tr>
<tr>
<td>0.28</td>
<td>25.17</td>
<td>10.4</td>
</tr>
</tbody>
</table>

The influence of residual water cement ratio on temperature during CO$_2$ curing is very obvious. When the residual water cement ratio is 0.14 ~ 0.20, the peak value of temperature curve is up to 67, which is conducive to rapid reaction.

Fan Yongfa and others believe that the concepts of water cement ratio and strength of concrete are closely related. The lower the water cement ratio of concrete, the higher its strength and the higher the compactness of concrete; vice versa. The larger the water cement ratio, the smaller the amount of cement per unit, the less the content of Ca (OH)$_2$ per unit volume of concrete, and the faster the carbonation speed. The permeability of concrete is affected by water cement ratio. Under the condition of a certain amount of cement, increasing the water cement ratio will increase the porosity of concrete, reduce the compactness, increase the permeability and increase the carbonation rate. At the same time, the influence of water cement ratio on concrete is also restricted by relative humidity. Cement slurry with low water cement ratio absorbs more carbon dioxide under low relative humidity (less than 40%). On the contrary, the relative humidity of concrete under water is higher than that under ash (60%).

3.2 Aggregate

Cheng Xiongfei found that the gradation and variety of selected coarse and fine aggregates have a great impact on the curing effect during concrete molding. The permeability of the interface between aggregate and cement slurry generally increases with the increase of aggregate particle size, and carbon dioxide is easier to diffuse in the curing process, so as to strengthen the curing effect.

3.3 Carbon dioxide curing conditions

2.3.1 carbon dioxide concentration

Sormeh et al. Predicted the CO$_2$ absorption under different experimental conditions by establishing a mathematical model. The results show that increasing the CO$_2$ concentration can accelerate the early CO$_2$ absorption of concrete, but it has no significant impact on the degree of CO$_2$ curing. Chen studied the effect of CO$_2$ concentration on carbonation depth and compressive strength of concrete. In Figure 5, the carbonation depth of concrete increases with the increase of CO$_2$ concentration under the same carbonation conditions. The higher the CO$_2$ concentration, the greater the internal and external concentration gradient, and more CO$_2$ can diffuse into the concrete and react with the hydration products in the concrete. With the increase of CO$_2$ concentration, the growth rate of carbonation depth decreases. The carbonation depth of concrete is negatively correlated with the strength grade of concrete.
2.3.2 carbon dioxide pressure

Shi et al. found that the CO2 pressure first increases and then basically remains unchanged on the curing degree of concrete. When the CO2 pressure is greater than 0.2MPa, the curing degree of concrete by CO2 will not increase even if the CO2 pressure is increased. Tang verified the above conclusion more intuitively by establishing the mathematical model of carbon dioxide storage of cement slurry during pressurized CO2 curing.

Shamsad Ahmad studied the influence of carbonation pressure and duration on the strength evolution of accelerated carbonation cured concrete, and found that in the process of ACC (accelerated carbonation cured concrete), the compressive strength of concrete increased with time, but the speed decreased. As shown in Figure 4, carbonization curing at 60 psi (414 kPa) for 10 hours has the best performance in strength increase and carbon dioxide absorption.

3.4 Pre curing

The moisture content of the specimen after pre curing is the key factor in the CO2 curing process. The pre curing process is essentially a water loss process. Studies have shown that the pre curing time has little impact on CO2 curing, and the CO2 curing degree of concrete is mainly improved by adjusting the water content. Pre curing can improve the reaction degree of carbon dioxide curing of concrete.

Fan Yongfa and others found through the research on the carbonation performance of concrete that properly prolonging the early wet curing time can improve the hydration degree of cementitious materials in concrete and increase the compactness of concrete surface layer.

Hassan et al. found that the free water on the concrete surface hinders the absorption of CO2. After pre curing, the absorption capacity of concrete to CO2 is enhanced. Therefore, the degree of CO2 curing is improved. During pre curing, the water loss rate of concrete needs to be controlled. If the water loss rate is too large, the concrete specimen will produce plastic cracks.

However, Zou Qingyan pointed out that the influence of different pre curing time on the carbon dioxide curing degree of specimens is not regular, but with the different pre curing environment, the change of pre curing time will have different effects on the carbon dioxide curing degree of specimens.
4. Effect of carbon dioxide curing on concrete performance

4.1 Mechanical properties

C-S-H gel is the main hydration product of concrete and the source of strength of concrete. According to different Ca / Si ratio, it can be divided into C-S-H (Ⅰ) type with low Ca / Si ratio and C-S-H (Ⅱ) type with high Ca / Si ratio. C-S-H (Ⅰ) type is layered structure; C-S-H (Ⅱ) is a calcium silicate hexahydrate structure, and their molecular structures are shown in Fig. 5. Macroscopically, it makes the concrete structure compact and the compressive performance increases.

Zou Qingyan studied the influence of carbon dioxide curing degree on the compressive strength of concrete. It is found that there is a certain relationship between the two.

![Fig.5 Schematic of structure of C-S-H gel: (a) C-S-H (I); (b) C-S-H (II)](image)

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![Fig.6 Effect of degree of CO2 curing on compressive strength of specimen](image)

Fig. 6 is the relationship curve between carbon dioxide curing degree and compressive strength of the specimen. It can be seen from Figure 6 that with the increase of carbon dioxide curing degree, the compressive strength of the specimen also increases. When the carbon dioxide curing degree is 0 ~ 15%, the compressive strength of the specimen increases little; However, when the carbon dioxide curing degree exceeds 15%, the compressive strength of the specimen increases greatly. Because in the process of carbon dioxide curing, due to the chemical reaction inside the concrete specimen, sufficient calcium carbonate is generated to fill the pores of the concrete, which enhances the compactness of the concrete and improves the strength of the specimen.

4.2 Microstructure

After carbonization of hardened cement paste, the porosity of hardened paste is reduced, the pore structure is optimized, and the compactness of matrix is enhanced. The research shows that carbon dioxide surface treatment can improve the permeability and pore structure of concrete surface. After
carbon dioxide surface treatment, the porosity of concrete surface is reduced, and the permeability coefficients of gas, water and ions are reduced.

The micro morphology of cement paste will change during CO₂ curing. After CO₂ curing, the reaction generated calcium carbonate particles and silica gel fill the pores of concrete, making the concrete structure more compact and the performance enhanced. The SEM images of CO₂ cured and normal hydrated slurry are shown in Fig. 7(a) and Fig. 7(b) respectively.

EDS analysis shows that the content of carbon and calcium in the two crystals is very high, but the content of silicon is low, so it shows that calcium carbonate crystals are formed after CO₂ curing. In addition, C-S-H gel was found in two curing conditions. In the normal hydration slurry, the microstructure was mainly composed of amorphous C-S-H gel, and after CO₂ curing, the calcium carbonate crystal and C-S-H gel interlaced to form a tight structure.

4.3 Durability

Microstructure will affect the durability of concrete. After CO₂ curing treatment, the internal porosity of concrete is reduced, the structure is more compact, the hardness and density are improved, and the freeze-thaw resistance and weathering resistance are enhanced.

Junior et al. Studied the mechanical properties and pore structure characteristics of high and early strength concrete cured with CO₂, and found that the mechanical properties of concrete cured with CO₂ for 1H have been improved, and the concrete has higher hardness and density, reduced porosity, and its durability may be better. Zhang and others' research on the carbonation resistance of concrete after CO₂ curing shows that the subsequent hydration after CO₂ curing maintains a high pH value of concrete, and the carbonation resistance of concrete after CO₂ curing is close to that of normal curing concrete.

5. Conclusion

As a new concrete curing method, CO₂ curing concrete technology can not only improve the performance of cured concrete, but also be economical and environmental friendly. Through the review and analysis of existing research results, this paper draws the following conclusions:

(1) CO₂ curing concrete technology is a green, low-carbon and new curing concrete technology that enables the carbonatable cement in fresh concrete and the calcium silicate in cement clinker to react with CO₂ to produce calcium carbonate and silica gel.
(2) CO₂ curing concrete is mainly made of raw materials such as aggregates; Water binder ratio; Effects of CO₂ concentration and pressure and pre curing.

(3) After CO₂ curing, the micro morphology of concrete changes significantly. The surface of cement particles and slurry is covered with calcium carbonate crystals and silica gel. The formed silica gel and calcium carbonate are intertwined, and the total porosity of concrete is reduced, making the microstructure more dense.

(4) After CO₂ curing, the internal porosity of concrete is reduced, the structure is more compact, the hardness and density are improved, and the durability of freeze-thaw resistance, weathering resistance and sulfate resistance are enhanced.

6. Outlook

Based on the current understanding of the curing process, action mechanism and performance of CO₂ curing concrete technology. This paper puts forward the following prospects for the research of CO₂ curing concrete technology:

(1) In the process of CO₂ curing, pre curing is often used to improve the degree of CO₂ curing. How to reasonably and effectively control the water content in actual production and improve the degree of CO₂ curing concrete; How to optimize the process of CO₂ curing technology, that is, to further improve the degree of CO₂ curing concrete on the premise of ensuring the performance of concrete, needs to be deeply studied.

(2) Using carbon dioxide to cure concrete can shorten the production cycle of concrete products and improve the production efficiency. However, the actual production research shows that the utilization rate of CO₂ is not high, and improving the utilization rate of CO₂ in the use process needs to be developed urgently.

(3) At present, some technical means can estimate the content of carbon dioxide stored in cement-based materials through mass increment and heating, but the accuracy is not high. It is also a hot spot to study an accurate and efficient method to measure the amount of carbon dioxide stored.

(4) The CO₂ maintenance technology used at this stage needs to add new equipment and processes, resulting in high cost of CO₂ maintenance; Aiming at the field of utilization, reduce the capture cost of CO2 and make it widely popularized in the use industry.

(5) Exploring the application of CO₂ curing concrete technology in other cement-based composites will become a new research direction.

At the same time, we should also recognize that China is still in the stage of industrialization development, industrialization and urbanization continue to advance, carbon dioxide emissions will increase in a certain period of time, and the investment in CO₂ curing concrete, a green and low-carbon technology, will also increase.

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