Carbon curing of concrete: process overview and concrete properties

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Abstract

In response to the pressing problem of climate change caused by high greenhouse gas emissions from industrial processes, the European Union has set itself ambitious targets with the European Green Deal to achieve net-zero greenhouse gas emissions by 2050. The cement industry alone is responsible for 5 to 7 % of these emissions. One of the EU's strategies to reduce uncontrolled CO_2 emissions is the capture and utilisation of CO_2. This article provides a comprehensive overview of the carbon curing process, focussing on the mechanical properties and durability of carbon cured concrete. It examines the effects of various parameters such as CO_2 concentration, exposure time and concrete mix composition on optimising these properties to improve the process and effectively control changes in the properties of concrete products.

Ključne riječi: carbon curing, mechanical properties, durability properties, accelerated carbonation

Njegovanje betona ugljikovim dioksidom: pregled procesa i svojstava

Sažetak

Kao odgovor na hitan problem klimatskih promjena uzrokovanih visokim emisijama stakleničkih plinova iz industrijskih procesa, Europska unija postavila je ambiciozne ciljeve s Europskim zelenim planom kako bi postigla nulte emisije stakleničkih plinova do 2050. godine. Sama cementna industrija odgovorna je za 5 do 7 % tih emisija. Jedna od strategija EU za smanjenje nekontroliranih emisija CO_2 je hvatanje i korištenje CO_2. Ovaj članak pruža sveobuhvatan pregled procesa karbonizacije betona, s naglaskom na mehanička svojstva i trajnost karboniziranog betona. Ispituje učinke različitih parametara kao što su koncentracija CO_2, vrijeme izlaganja i sastav betonske smjese na optimizaciju tih svojstava kako bi se poboljšao proces i učinkovito kontrolirale promjene u svojstvima betonskih proizvoda.

Key words: njegovanje betona ugljičnim dioksidom, mehanička svojstba, trajnosna svojstva, ubrzana karbonizacija

1 Introduction

Climate change is a consequence of increasing greenhouse gas emissions. The 2018 EU directive "A Clean Planet for All" [1] predicts climate change for all EU regions, Mediterranean, continental and mountain regions. With strategies such as the Green Deal [2] and the Paris Agreement [3], the EU aims to achieve climate neutrality by 2050. The construction industry is responsible for 40 % of total CO_2 emissions [4], i.e. around 15 gigatonnes per year [4], and around 10 billion tonnes of waste [5]. Every day, 198.000 tonnes of concrete waste are produced, 95 % of which is used as aggregate for new concrete [6]. Annual cement production amounts to 4.1 billion tonnes [7], which accounts for around 5-7 % of total CO_2 emissions [8]. The high greenhouse gas emissions in cement production are due to the high temperatures (approx. 1450 °C) and the calcination process of the limestone.

The cement industry is still considered "hard to abate", but progress is being made through various strategies such as reducing the amount of clinker in cement through mineral additives, continuously improving energy efficiency, switching to low-carbon fuels and better utilisation of materials. Currently, the greatest efforts to reduce emissions are being invested in new technologies for carbon capture and storage (CCS) and utilisation (CCU). CCS captures and stores CO_2 from emission sources, while CCU utilises the CO_2 to produce useful materials or products. It is estimated that the EU will be able to capture at least 320 million tonnes of CO_2 by 2050, of which 55 % will be used in products and the rest will be stored [9]. A particular focus is on the integration of captured CO_2 into the production process of concrete. It is estimated that by 2050, 0.1-1.4 gigatonnes of CO_2 could be used in this way instead of being released into the atmosphere[10]. The aim of this manuscript is to give a comprehensive overview of the possibilities for achieving equivalent or even better mechanical properties of CO_2-treated concrete, known as carbon curing.

2 Process of concrete carbon curing and properties of final product

Weathering carbonation differs from the carbonation hardening of concrete. Weathering carbonation is a process that occurs naturally over time in hardened concrete. During this process, atmospheric CO_2 reacts with hydration products of the concrete, such as calcium hydroxide ($Ca(OH)_2$), to form calcium carbonate. Curing with CO_2 is a process that aims to simultaneously reduce emissions and produce concrete products with satisfactory mechanical and durability properties by exposing the concrete to high concentrations of CO_2. Carbon curing results in the formation of C-S-H gel and calcium carbonate ($CaCO_3$) as a product of the

reaction between CO_2 and the calcium silicates in the Portland cement [11]. The curing process is critical in concrete production as it controls moisture loss to achieve the desired mechanical and physical material properties. The use of CO_2 for cement activation offers an alternative to the traditional curing methods using water or steam proposed by Berger in the 1970s [12]. Portland cement contains 80 % calcium silicates [13], with alite (C_3S) and belite (β -C_2S) predominating. Alite is the predominant mineral in clinker, which is crucial for the development of cement strength, although cement production consumes a significant amount of lime and requires higher sintering temperatures, which increases production costs. In contrast to C_3S, β-C_2S does not require higher sintering temperatures and the amount of lime used in the production of β-C_2S cements is lower, making β-C_2S an investigated alternative to reduce emissions. The disadvantages of belite include its lower hydration activity compared to alite, resulting in a slower reaction with water, which can lead to a longer time to reach the desired strength of the cementitious mass and lower early strength. The early-age carbon curing process of concrete is described by equations 1-4 [14].

$$C_3S + (3-x)CO_2 + yH_2O \rightarrow C_xSH_y + (3-x)CaCO_3 \tag{1}$$

$$C_2S + (2-x)CO_2 + yH_2O \rightarrow C_xSH_y + (2-x)CaCO_3 \tag{2}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{3}$$

$$C\text{-}S\text{-}H + 2CO_2 \rightarrow SiO_2 + 2CaCO_3 + H_2O \tag{4}$$

The reaction of calcium silicates with CO_2 is faster than hydration, in which calcium silicates react with water to form hydrate products, which are responsible for the strength of the concrete. Under conditions where CO_2 is present, carbonation can begin before hydration, which allows for faster development of concrete strength than hydration alone [15]. This process is very complex due to many influencing factors such as water-binder ratio, pre-curing, pressure, CO_2 concentration, preparation, concrete raw materials, etc.

2.1 Laboratory process of carbon curing of concrete

The laboratory process of CO_2 curing of concrete consists mainly of 3 phases: pre-curing, carbonation and post-curing [16]. Pre-curing involves curing in and outside the mould at 20-25°C and 40-60 % relative humidity [17]. In-mould curing takes place after the concrete mix has been placed to ensure that it hardens before demoulding. During demoulding, the samples are removed from the mould to increase the water evaporation surface and allow better CO_2 diffusion

during the carbonation phase. The w/s ratio is crucial, because too much water can hinder the diffusion of CO_2, while too little can stop the reaction. A higher w/s ratio is usually used in the pre-curing phase as there is a continuous loss of water during demoulding curing, which leads to increased CO_2 uptake in later phases, but this stabilises once 40 % of the water has been consumed [17]. The carbonation phase is the phase in which the concrete is exposed to CO_2 and there are two types of reaction systems: enclosed and flowable chambers. The enclosed system is more efficient as it can withstand higher partial pressures of CO_2. Due to precise control, laboratory experiments are performed in enclosed chambers where samples are usually exposed to CO_2 at a pressure of 1 to 5 atm, where the influence of temperature and relative humidity is very important. The preferred temperature is between 20 and 25 °C, the relative humidity between 60 and 70 % [17]. Post-curing after carbonation allows further hydration of the remaining unreacted hydraulic phases. It is important to compensate for the lack of water caused by the pre-curing process and carbonation in order to ensure the hydraulic reaction and thus higher strength.

2.2 Mechanical properties of carbon-cured concrete

Exposing concrete to high levels of CO_2 under controlled conditions aims to accelerate the natural process of carbonation, achieve maximum storage of CO_2 within concrete, but also aims to create a building material with improved mechanical and durability properties. This approach has already proven successful in the treatment of various types of binders, including those based on classical Portland cement [18, 19], calcined limestone and sand [20] as well as concrete with recycled aggregates [21].

The compressive strength of carbon-cured concrete depends largely on the water-cement ratio, the porosity and the properties of the coarse aggregate [22]. In their work, Li et al. compared CO_2-treated concrete with moisture-cured concrete and concluded that the compressive strength of CO_2-treated concrete is 10 % higher than that of moisture-cured concrete of the same age (see Figure 1) [22]. Concrete with carbonated recycled aggregate has a higher compressive strength than concrete with non-carbonated recycled aggregate and is capable of absorbing 7.9 kg CO_2 per tonne of aggregate [23]. An 11.8 % increase in the volume of the solid phase in concrete with recycled aggregate indicates a higher density and a stronger structure [23]. Monkman et all. [24] compared the effects of conventional accelerating admixtures and CO_2 on the durability properties of concrete and on its fresh and hardened concrete properties. When testing different doses of CO_2, they found that the optimum dose reduced the setting time by 40 % and increased the compressive strength after one and three days by 14 % and 10 % respectively. It was found that CO_2 injection accelerated hydration,

shortened setting time and increased the strength of the concrete, while having no negative effect on durability. The average acceleration of the setting time was 25 %, while the final setting was accelerated by 23 %. Economically, the use of CO_2 as an accelerator is more cost-effective compared to conventional accelerators. Tiefeng Chen et al. [25] investigated the influence of pre-curing and carbonation time on the properties of the cement paste, focusing on compressive strength and microstructure. The results show that hydration and carbonation reduce the porosity of the cement paste, with carbonation reducing the larger pores and hydration reducing the smaller pores. The research results show that carbonation increases the strength of the hardened cement paste in the initial phase, but that this influence decreases over time. The optimum pre-hardening time is reached when 30-40 % of the water has been lost from the cement paste. It should be noted that the longer the carbonation time, the shorter the recommended pre-hardening time. The results also suggest that the hydration reaction rate can be reduced during the carbonation process as a carbonate layer forms on the cement surface, which acts as a barrier to further hydration. In addition, competition for available calcium ions may slow hydration, and higher CO_2 concentration may slow hydration as it may bind calcium ions destined for hydration. Salman Siddique et al. [26] investigated the influence of the water-cement ratio on the physico-chemical and microstructural properties of high-belite cement during carbonate curing. The results show that an increase in the water-cement ratio increases CO_2 absorption, promotes the consumption of the belite phase and facilitates calcite formation. A higher water-cement ratio leads to a higher compressive strength, which indicates a more intensive carbonation and microstructural compaction.
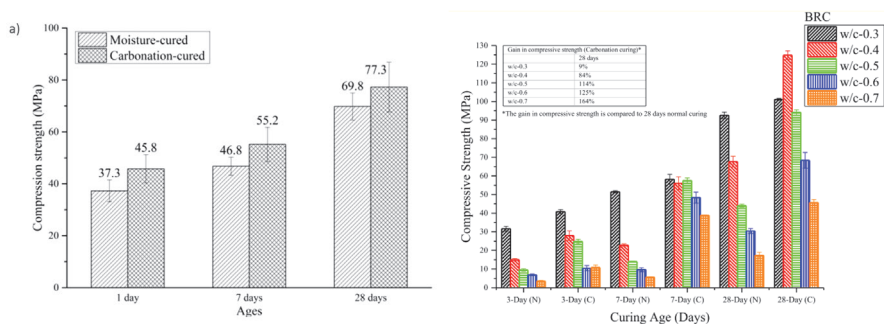

Figure 1. a) Compressive strength of carbonation-cured and moisture-cured samples [27], b) Compressive strength of normally cured and carbonation cured belite-rich cement with varying water to cement values [26]

2.3 Durability properties of carbon-cured concrete

Previous studies reported reduced porosity of carbon-cured concrete, which protects against the penetration of chloride ions, increased resistance to harmful external influences such as sulphates and acids and reduced weather-related abrasion and damage caused by freezing and thawing [15]. However, the corrosion resistance of steel in carbonated concretes remains a challenge [27]. Previous studies have shown that the reaction of CO_2 and Ca(OH)2, during the carbonation process leads to a drop in pH. Some studies suggest that prolonged exposure to CO_2 increases the resistance to chloride penetration as the porosity decreases due to the hydration reaction and the denser microstructure [28]. The conclusion from the research by Zhang et al. [14] is that carbonation in the early stage of concrete can be beneficial. Carbonation lowers the surface pH to 9.2 but keeps the core pH above 12. Subsequent hydration raises the surface pH to above 12.3, making the surface of the concrete less permeable and more resistant to weathering carbonation. This process enables the development of a layered structure with a carbonate layer on the surface, which improves the strength and durability of the concrete. On the other hand, although the pH value can partially recover to values above 12 with suitable post-curing hydration, a lower $Ca(OH)_2$ content makes the concrete more susceptible to corrosion due to ageing carbonation during its service life [17]. Lower pH conditions also promote the mobility of chloride ions by reducing the binding capacity and thus facilitating their transport into the concrete. While previous research indicates accelerated corrosion of steel at reduced pH, experience shows that lowering pH alone is not sufficient to cause significant steel corrosion in concrete, since the occurrence of several other parameters is needed [29]. Nevertheless, long-term durability of carbon-cured concrete remains important question for further real scale application.

3 Conclusion

Tackling climate change requires urgent action to reduce greenhouse gas emissions, particularly in industries such as construction that contribute significantly to CO_2 emissions. The introduction of carbon curing techniques in concrete production is a promising way to reduce emissions while improving material properties. It is estimated that up to 1.4 gigatonnes of CO_2 could be sequestered in concrete by 2050, contributing to global efforts to reduce emissions. Research shows that optimising CO_2 dosage can reduce setting times, increase initial and final strength and improve cost efficiency compared to conventional accelerators.
Among the many benefits of carbonation, one of the biggest challenges is ensu-

ring corrosion resistance. While previous research indicated accelerated corrosion of steel in concretes with reduced pH, experience shows that pH reduction alone is not sufficient to achieve corrosion and that parameters such as changes in moisture over time, depth of cover and the microstructure and chemical composition of the pores in the carbonated matrix at the interface between steel and concrete are much more important. Further research is needed to better understand the relationship between the macroscopic properties and the microstructure of the material in order to optimise the CO_2 curing process and control changes in concrete properties.

Acknowledgment

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