

Research on the Mechanisms of Carbon Sequestration in Building Cement

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Abstract:

Global carbon emissions have long been a critical issue concerning climate change and environmental sustainability. With the accelerating pace of global industrialization and urbanization in recent years, carbon emissions have continued to rise, becoming a major source of greenhouse gas emissions. Cement production is a significant contributor to carbon emissions; thus, finding methods to reduce carbon emissions from cement is crucial. Carbon sequestration technology in cement-based materials involves permanently storing CO₂ within cementitious materials by utilizing carbon aggregates in cement or absorbing CO₂ during the production process, thereby mitigating carbon emissions. In recent years, various carbon sequestration technologies have emerged, with carbonation curing being a prominent trend. This technology not only facilitates CO₂ absorption by cementitious materials but also enhances their mechanical properties and durability, albeit with certain challenges. Therefore, exploring new directions for CO₂ absorption by cement-based materials is an urgent issue to address. Furthermore, the carbon sequestration mechanism of cement pastes is investigated.

Keywords: cement; CO₂; carbon sequestration mechanism

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I. Introduction

Since the onset of the Industrial Revolution in 1760, human activities and the combustion of fossil fuels have emerged as significant contributors to climate change. In recent years, there has been a notable increase in greenhouse gas emissions, with carbon dioxide (CO₂) accounting for 82% of total greenhouse gas emissions and exerting the most significant greenhouse effect. Consequently, CO₂ has become the primary pollutant among the six greenhouse gases. Prior to the Industrial Revolution, the level of CO₂ was approximately 280 ppm. However, atmospheric CO₂ concentrations have now risen to 413 ppm.

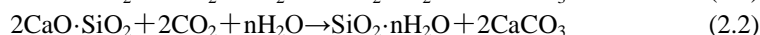
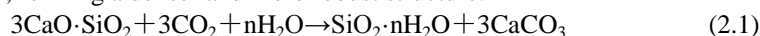
The variety of CO₂ mitigation technologies includes carbon capture, utilization, and storage (CCUS), which has been internationally recognized in recent years as the most effective and promising method for reducing CO₂ emissions. CCUS technology is an extension of carbon capture and storage (CCS) technology. While CCS technology can be used for large-scale carbon reduction, it suffers from high energy consumption. In contrast, CCUS technology specifically involves separating and capturing low-concentration CO₂ emissions, purifying them into high-concentration CO₂, and then storing or recycling them for the production of fuels, chemicals, or carbonate products. The advantage of CCUS technology over CCS lies in the resource utilization of CO₂, significantly reducing production costs. CO₂ capture involves the process of separating and enriching CO₂ through various technical means, which can be categorized into pre-combustion capture, post-combustion capture, and oxy-fuel combustion, depending on their technical characteristics. CO₂ transportation is an intermediate step in CCUS technology and includes land, maritime, and pipeline transportation. The primary CO₂ storage technologies are geological storage, ocean storage, and mineral storage. Geological and ocean storage offer large storage capacities but carry risks of leakage. Mineral storage, which involves the reaction of CO₂ with alkaline metal oxides to produce stable carbonates, is considered the most stable, safe, and economical method. CO₂ utilization can be classified based on its physical and chemical properties into geological utilization, chemical utilization, biological utilization, mineralization utilization, and energy utilization.

II. Chemical Carbonation Mechanism of Cement Paste

2.1 Mineralogical Composition of Cement Clinker

The hydration degrees of C₃S, C₂S, C₃A, and C₄AF in cement clinker after 28 days of curing are reported as 91%, 67%, 96%, and 79%, respectively [1]. Consequently, in most cases, the onset of carbonation reaction significantly precedes the completion of hydration reactions. C₃A and C₄AF exhibit minimal reactivity with CO₂ gas, while early-stage carbonation reactions of C₃S and C₂S yield CaCO₃ and C-S-H gel [2]. However, in the final stages, they result in the formation of CaCO₃ and amorphous SiO₂ gel, as depicted in Equations 2.1 and 2.2. The

CaCO₃ crystals, along with unreacted C₃S and C₂S particles, act as a framework, while the amorphous SiO₂ serves as a binder, forming a denser and more robust structure.



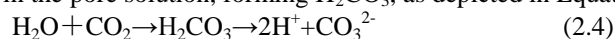
2.2 Calcium hydroxide (Ca(OH)₂)

In numerous studies, the carbonation reaction in cured cement paste is expressed by Equation 2.3.

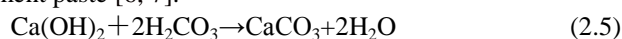


The occurrence of this reaction is attributed to calcium being the most prevalent element in silicate cement hydrates, and Ca(OH)₂, compared to other calcium compounds, exhibits the highest solubility in water. Therefore, its reaction with CO₂ ensues readily. However, the dissociation of Ca(OH)₂ and CO₂ dissolved in the pore solution is a prerequisite for carbonation. Equation 2.3, however, only applies to describe the carbonation reaction of Ca(OH)₂ in ideal conditions in aqueous solutions; hence, it is insufficient to elucidate the carbonation mechanism of cured cement paste.

It is well-established that carbonation reactions in cement paste occur within the capillary pores, which are filled with pore solution characterized by a high pH, while Ca(OH)₂ predominantly exists in a solid state [3]. The pore solution comprises various cations such as sodium and potassium, along with balanced hydroxide ions, with relatively low concentrations of Ca²⁺ [4]. Consequently, the elevated pH of the pore solution in cement paste is highly dependent on the concentration of Na⁺ and K⁺ ions in equilibrium with OH⁻ [5]. CO₂ from external sources infiltrates and dissolves in the pore solution, forming H₂CO₃, as depicted in Equation 2.4.



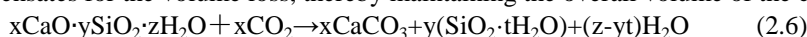
The dissolution of Ca(OH)₂ in the pore solution can react with H₂CO₃ to produce precipitates of CaCO₃ with lower solubility, as illustrated in Equation 3.5. Moreover, this reaction facilitates the decomposition of solid Ca(OH)₂, maintaining the equilibrium between alkali metal ions and OH⁻ in the pore solution. As the reaction progresses, the content of Ca(OH)₂ in the cement paste decreases while the content of CaCO₃ increases, consequently reducing the pH of the cured cement paste [6, 7].



2.3 Calcium silicate hydrate (C-S-H)

Portland cement generates various hydration products through the hydration process, including calcium silicate hydrate (C-S-H). The proportions of these hydration products vary depending on the composition of the cement; however, in most cases, the proportion of amorphous C-S-H gel is highest. Generally, the carbonation reaction of C-S-H begins only when a sufficient degree of carbonation is attained, typically after the majority of Ca(OH)₂ has been consumed [8].

Due to the uncertain stoichiometry of C-S-H, the carbonation reaction of C-S-H gel can be represented by Equation 2.6. The molar volume of the reaction product, the silicate gel, is smaller than that of the uncarbonated C-S-H, which may result in shrinkage of the cement paste. However, the generation of CaCO₃ precipitates compensates for the volume loss, thereby maintaining the overall volume of the cement paste unchanged [9].



As CO₂ permeates into the voids and capillaries within the cement matrix, it reacts with Ca(OH)₂ present in the cement gel to form CaCO₃. Due to the low solubility of CaCO₃, precipitation occurs. To ensure the constant concentration of Ca²⁺ and OH⁻ in the pore solution, Ca(OH)₂ originally present in the solid phase dissolves to maintain the equilibrium amount of Ca²⁺. Additionally, the product layer formed by CaCO₃ deposition on the capillary pore walls restricts the rate of reaction between CO₂ and the alkaline components within the cement particles but does not impede the ultimate carbonation process of the cement paste. With continued diffusion of CO₂ and the presence of CO₂ bubbles, CO₂ continues to react with Ca(OH)₂, leading to a gradual decrease in Ca(OH)₂ content and consequently a decrease in the alkalinity of the cement paste.

During the initial hydration of cement, the reaction between cement and water forms C-S-H gel. As the paste begins to set, moisture within the hardened cement with CO₂-filled voids gradually evaporates, resulting in the eventual formation of multiple pores of various sizes and shapes. For cement pastes prepared via carbonation curing, a portion of CO₂ is absorbed and reacts with Ca(OH)₂ within the paste to form CaCO₃ before the fresh paste is formed, thereby augmenting the hydration products of cement. Upon hardening of the paste, the relative reduction in internal pore area leads to a decrease in the amount of CO₂ within the pores.

III. Conclusions

The process of CO₂ adsorption by cement paste mainly involves two aspects: 1. The diffusion of CO₂ gas within the cement paste and the physical sequestration of CO₂ by cementitious materials. 2. The adsorption of CO₂ by cementitious materials, including the adsorption of CO₂ by cement clinker minerals, calcium hydroxide, calcium silicate hydrates, and calcium aluminate hydrates.

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