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ENHANCEMENT OF CEMENT MORTAR HYDRATION BY CARBONATION ACTIVATOR INDUCED BY ORGANIC ADDITIVES

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Abstract: This study developed an efficient in-situ carbonation activator with enhanced carbon capture, using organic additives in an aqueous solution. The fresh carbonated cement suspension was mixed with raw materials through secondary mixing to improve cement mortar hydration. Various organic additives were tested for their ability to leach calcium and aluminum ions, affecting carbonation efficiency and products. Characterization showed that these additives increased carbon capture and influenced calcium carbonate morphology. The activator, rich in silica gel and calcium carbonate polymorphs, acted as a filler and nucleating agent, accelerating hydration and promoting carboaluminate formation. This method reduced mortar porosity, improved pore structure, and enhanced mechanical strength while achieving effective carbon sequestration.

1 INTRODUCTION

The global community is actively working to mitigate the greenhouse effect, primarily caused by the substantial release of carbon dioxide since the Industrial Revolution, with the construction industry heavily reliant on carbon-intensive Ordinary Portland Cement (OPC) as a key component of modern infrastructure [1]. Given that cement production accounts for approximately 8% of total anthropogenic CO_2 emissions [2, 3], it is crucial to develop scalable solutions to reduce the environmental impact associated with concrete production.

The persistent presence of unhydrated cement in hardened concrete, even after extended water immersion, presents an opportunity to reduce the carbon footprint of concrete production by enhancing cement hydration [4]. Therefore, an appropriate cement activation strategy is sought to enhance the degree of cement hydration, thereby improving its strength efficiency and extending the lifespan of infrastructure, which, from a life-cycle perspective, contributes to reducing the carbon footprint. Traditional methods to activate cement reactivity include thermal, mechanical, and chemical activation [5-7]. However, these methods have limitations, such as reduced ultimate strength at higher curing temperatures, diminishing returns from increased surface area, and compromised long-term performance due to chemical additives.

Recently, admixtures such as reactive silica, calcium-silicate-hydrate seeds [8, 9], and calcium carbonate [10-12] have shown potential in activating cement binders. Despite their benefits, high costs and stability issues have limited their practical application. The carbonation of OPC offers a promising alternative, as its primary clinker phases react with CO_2 to form calcium carbonate and silica gel, which exhibit pozzolanic properties [13-

15]. However, controlling the polymorph formation and stabilization in carbonated cement composites remains challenging.

The study involves two main stages: the production of the activator and the in-situ activation of concrete via secondary mixing. The first stage examines the impact of organic additives on CO_2 sequestration efficiency and the mineralogical composition of the activators. The second stage evaluates the compressive strength, microstructures and the phase of the activated cement mortar. This approach seeks to introduce highly reactive submicron /nanoscale calcium carbonate and silica gel into concrete efficiently, potentially bypassing the costly dispersion of solid nanomaterials.

2 EXPERIMENTS AND MATERIALS

2.1 Raw Materials

This research utilized Ordinary Portland Cement (OPC), specifically CEM 1 52.5, obtained from HK Green Island Cement Company. The chemical compositions of OPC are detailed in Tables 1. The particle size distributions of river sand is illustrated in Fig. 1. Glutamic acid (GLTA) and Ethylenediaminetetraacetic acid (EDTA), were sourced from Acros Organics. Deionized water and CO_2 gas with 99.9% purity were used throughout the experiments.

Table 1: Chemical composition of OPC (wt %)

OPC	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	Others
%	58.1	23.1	9.2	3.6	2.7	3.3

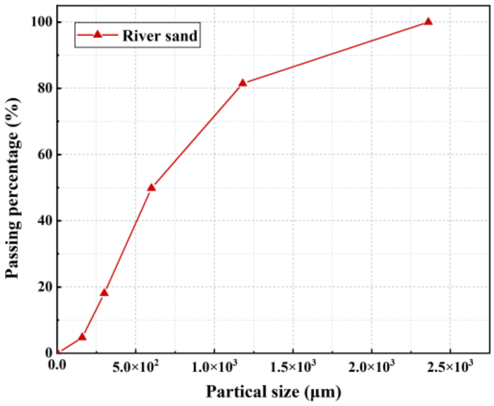

Fig.1 Particle size distributions of river sand.

2.2 Pre-mixing Process: Activator Preparation

To create CO_2-derived activators, termed "Pre-carbonation" batches, 150g of OPC was mixed with 250g of an aqueous solution, followed by CO_2 injection at 25°C under atmospheric pressure. The solution included organic additives and deionized water. GLTA and EDTA concentrations were set at 0.01 M and 0.005 M, respectively, based on their functional groups. Cement was added to the solution and stirred at 800 rpm, while CO_2 was injected at 1.5 L/min for 20 minutes. The CO_2 injection tube was placed below the liquid surface, with a diffuser ensuring uniform microbubble dispersion.

Thermogravimetric Differential Scanning Calorimetry (TG-DSC) assessed CO_2 capture. X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) analyzed structural and chemical compositions.

2.3 Secondary Mixing: Concrete Activation

After pre-mixing, activator was combined with remaining raw materials to cast cement mortar, as shown in Table 2, maintaining a water-cement ratio of 0.4 and a cement/sand ratio of 1:2. Mortars were cast into 40 × 40 × 40 mm^3 cubes for compressive strength testing.

Compressive strength was tested after curing in a saturated calcium hydroxide solution for 1, 3, 7, and 28 days. Mercury Intrusion Porosimetry (MIP) evaluated pore structure. Cement pastes samples, excluding sand, were prepared for X-ray Diffraction (XRD) to further investigate hydration effects.

3 RESULT AND DISCUSSION

3.1 CO_2-derived activator

In this study, the thermogravimetric of the activator was tested, with particular attention given to the thermogravimetric loss associated with the decomposition of calcium carbonate in the temperature range of 500-800°C. Based on the weight loss observed within this range, the CO_2 uptake rate was calculated. As shown in Fig. 2, the CO_2 sequestration amount of batch without organic additives during the pre-carbonation process can reach approximately 5% of the cement mass. With the assistance of organic additives such as EDTA and GLTA, the CO_2 uptake efficiency increased by approximately 35.8%. These observations indicate that the auxiliary carbonation facilitated by organic additives could enhance CO_2 uptake and carbonation efficiency.

Table 2 Mixture design

Mortar	Pre-mixed process				Secondary mixing process		
Mixture	OPC (g)	Water (g)	Chelator	CO_2	Water (g)	OPC (g)	Sand (g)
Reference	--	--	--	--	400	1000	2000
CPM	150	250	--	inject	150	850	2000
CPEM	150	250	EDTA	inject	150	850	2000
CPGM	150	250	GLTA	inject	150	850	2000

"Reference": the control group of cement mortar producedwith traditional mixing process.

"CPM" "CPEM" "CPEM": chelator-assisted pre-carbonation groups of cement mortar with CO_2.

The FTIR spectra (Fig. 3) reveal significant changes during carbonation, where Si-O asymmetric stretching vibrations in C_3S and C_2S phases shift from 916 cm^{-1} to a broader peak at 960 cm^{-1} after 20 minutes, indicating the formation of a C-S-H gel polymerization network [16]. The disappearance of the ν_3-SO_4^{2-} vibration at 1120 cm^{-1} suggests the transformation of ettringite into carboaluminate due to carbonation [17]. Additionally, the absence of the Al-OH absorption band at 844 cm^{-1} implies the incorporation of aluminum into the C-A-S-H gel rather than forming a separate alumina hydroxide gel. The presence of carbonate bands, particularly v_3-CO_3^{2-} between 1420 and 1480 cm−1, v_2-CO_3^{2-} at 874 cm^{-1}, and v_4-CO_3^{2-} at 712 cm^{-1}, confirms the formation of calcite and vaterite in the carbonated batches [18]. The FTIR analysis indicates that carbonated activator enriched with C-S-H / C-A-S-H gels and carboaluminate phases. Organic additives act as catalysts, promoting the formation of reactive polymorphs.

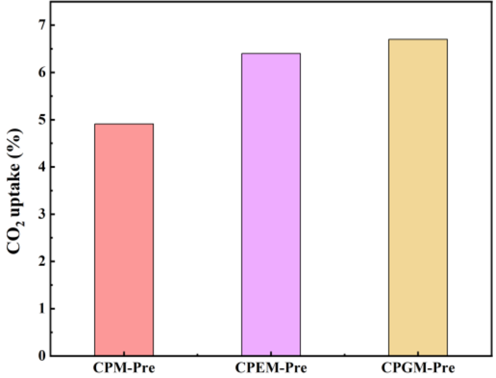

Fig. 2 CO_2 uptake of activator

XRD analysis (Fig. 4) further supports these findings, showing changes in the mineral composition after 20 minutes of pre-mixing. The Rietveld refinement quantifies the contents of various polymorphs, CPEM-Pre and CPGM-Pre contain less calcite but more vaterite, likely due to the reaction between Ca^{2+}-organic complexes and CO_3^{2-}, which favors vaterite formation, whereas direct Ca^{2+} and CO_3^{2-} reactions favor calcite. These findings align with the FTIR results, highlighting the role of organic additives in enhancing carbonation and CO_2 sequestration efficiency.

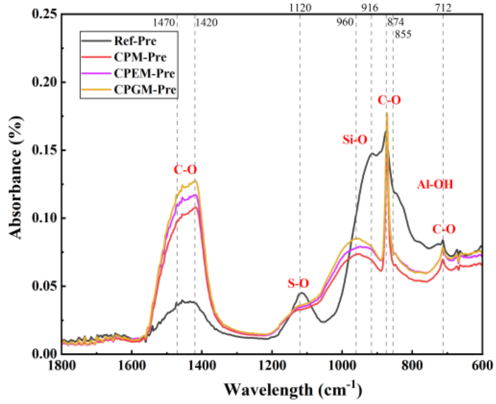

Fig. 3 FTIR of activator. Ref-Pre batch was not injected with CO_2 and organic additives but underwent the same mixing process.

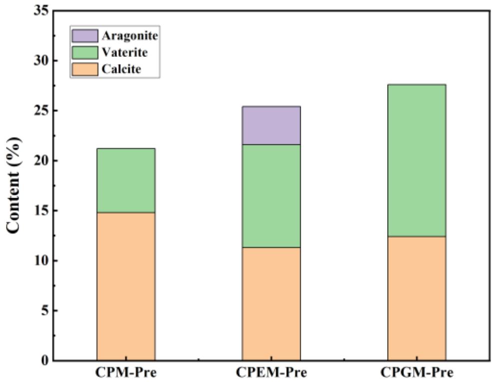

Fig. 4 Contents of calcium carbonate in activators

3.2 Activated cement mortar

Fig. 5 illustrates the early and late compressive strengths of various cement mortar batches. The incorporation of CO_2-derived activators significantly influences compressive strength, regardless of the curing age. Notably, CPM, CPEM, and CPGM exhibit varying degrees of strength enhancement compared to the Reference batch, with the most pronounced improvements being observed under the chelating agent-assisted pre-carbonation activation. As anticipated, CO_2-derived activators enhance strength, and the addition of organic additives further boosts carbonation efficiency.

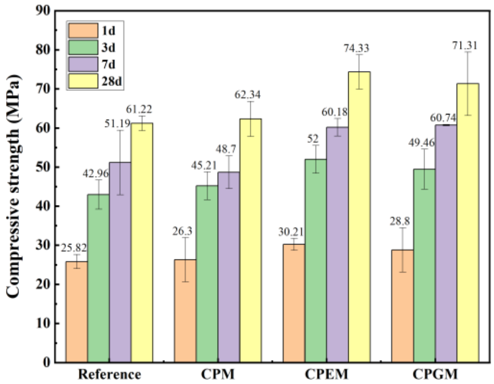

Fig.5 Compressive strength of cement mortar

Mercury intrusion porosimetry (MIP) results (as shown in Fig. 6) elucidate the total porosity and critical pore size of Reference, CPM, CPGM, and CPEM samples at 3 days of curing. Compared to the Reference batch, CPM, CPGM, and CPEM demonstrate reduced critical pore size and total porosity. This indicates that the incorporation of CO_2-derived activators promotes early hydration, refines the pore structure, and decreases porosity.

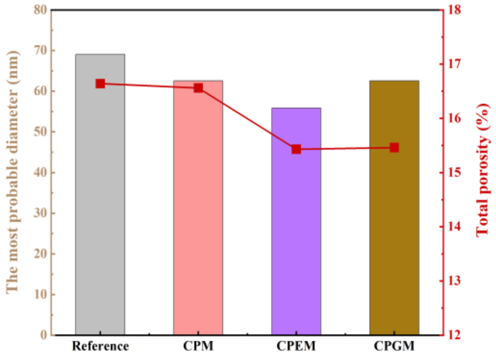

Fig. 6 Pore structure of cement mortar

Using Rietveld-refined quantitative X-ray diffraction (QXRD) analysis, the composition of the hydration products in cement mortar after 3 days was determined, as shown in Fig. 7. The findings indicate that CO_2-derived activators enhance the hydration of cement clinker. Specifically, the carbonation-activated samples exhibited distinct presence of hemicarbonate (Hc) and monocarbonate (Mc) phases, which were absent in the reference samples. Notably, cement mortars prepared with activators assisted by organic additives showed higher contents of Hc and Mc, along with an increase in the amorphous phase.

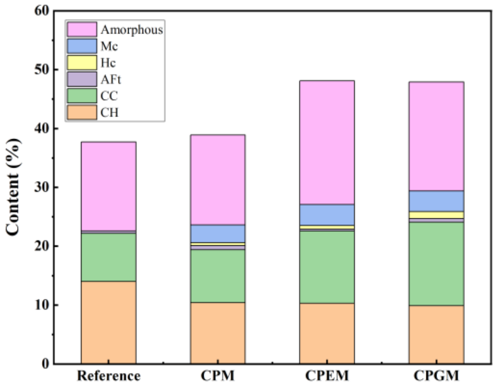

Fig. 7 Phase composition of cement mortar

This can be attributed to the activation effect of high levels of silica gel and highly reactive forms of calcium carbonate (CC), such as amorphous calcium carbonate (ACC) and vaterite, during the secondary mixing activation process. Silica gel provides nucleation sites for hydration, while finely dispersed calcium carbonate particles enhance hydration by acting as nucleation sites.

Additionally, the reaction between calcium carbonate and alumina phases influences the composition of sulfate reaction products, leading to the formation of carboaluminate phases [19,20].

4 CONCLUSIONS

This study investigates the enhancement of cement mortar hydration and mechanical properties using CO_2-derived activators, augmented by organic additives. This approach effectively improves cement hydration and addresses the dispersion challenges of additives encountered in traditional methods.

(1) The role of EDTA and GLTA in pre-carbonation is attributed to their strong chelating abilities, which accelerate calcium dissolution and $CaCO_3$ precipitation, thereby enhancing carbonation efficiency. This stabilizes the polymorphic forms of calcium carbonate, prevents particle agglomeration, and promotes the dispersion and stabilization of fine carbonated particles.

(2) CO_2-derived activators significantly enhance hydration during the secondary mixing process, improving the pore structure of cement mortar. The use of organic additives during carbonation further refines the pore structure, reduces porosity, and transforms harmful pores into harmless ones, thereby markedly increasing the degree of hydration and compressive strength of the cement mortar.

(3) Carboaluminates play a crucial role in the activated mortar, as these activators contain fine, highly reactive polymorphs of calcium carbonate, such as amorphous calcium carbonate and vaterite. These polymorphs enhance hydration by serving as nucleation sites and influencing the composition of sulfate reaction products.

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