



REVIEW ARTICLE

Magnesium Cements as Sustainable Alternatives to Portland Cement: Carbonation Mechanisms, Mechanical Performance, and Environmental Benefits

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ABSTRACT

The construction industry remains one of the major CO2 emission sources globally because producing Portland cement contributes to about eight percent of total emissions. Sustainable alternatives need development to address climate change effects because limestone calcination produces substantial CO2 emissions at high energy usage levels. Four types of magnesium cements which include Reactive Magnesia Cement (RMC) Magnesium Phosphate Cement (MPC) Magnesium Oxychloride Cement (MOC) and Magnesium Oxysulfate Cement (MOS) have proven viable alternatives due to their natural carbonation capacity that allows CO2 absorption. These concrete substitutes deliver better mechanical performance with increased strength together with enhanced durability and fire safety characteristics and they help reduce carbon emissions. The CO2 sequestration ability of Magnesium Cement increases tremendously through Accelerated Carbonation Curing (ACC) because the process enables formation of stable carbonates like magnesite and nesquehonite. The capture efficiency for CO2 embodied in RMC reaches 92% while PC captures only 50% thus resulting in improved emissions reduction outcomes. Rapid-setting MPC finds common use for infrastructure repairs because of its exceptional early strength yet MPC and MOC and MOS show top performance as fire-resistant materials and thermal insulation components. MOC and limited large-scale adoption present challenges to full-scale implementation due to their water susceptibility issues. The paper conducts an extensive examination of MC carbonation processes as well as their mechanical properties and environmental benefits while showcasing their viability as sustainable replacement for PC. Future investigations should work on enhancing carbonation process performance while improving water resistance and developing hybrid cement mixtures to quicken the shift toward environmentally sustainable building materials.

Keywords: Magnesium Cements, Carbonation Mechanisms, Mechanical Performance, Environmental Benefits, Sustainable Construction

Introduction

Elevated CO₂ emissions endanger Earth's natural ecosystems alongside human existence because elevated atmospheric CO₂ quantities link to global

climate instability and major environmental disruptions [1]. Higher CO₂ emissions now trigger damaging erratic weather patterns and ocean rise along with species extinction which create an immediate menace against environmental sustainability worldwide. Scientists agree that human behavior drives the excessive rise of atmospheric CO₂ levels. Greenhouse gas emissions increase because of industrialization and urbanization and deforestation processes which heightens dangerous climate impacts [2]. Different building sector raw material production creates major carbon dioxide emissions in the manufacturing process.

Research demonstrates that cement manufacturing generates the second most CO₂ emissions among industrial businesses worldwide representing more than twenty-five percent of total industrial polluting emissions. Total worldwide CO₂ emissions derive 8% from the cement industry which makes it one of the key elements leading to the existing global warming crisis [1–3]. The manufacturing method of Portland cement (PC) which has been vital in construction materials for generations serves as the main cause of emissions [4]. Research indicates demand for PC will continue to expand because worldwide infrastructure projects persist to grow [5]. Manufacturing polycarbonate (PC) requires intense energy use because more than 4.8 billion joules of energy need to produce one ton of PC [6].

The annual worldwide cement production figures showed 3.5 billion metric tons in 2020 but experts anticipate reaching 4.83 billion metric tons by 2050 [7]. The production increase of cement could result in temperature rises between 1.4°C and 5.8°C across the Earth surface. The PC sector produces CO_2 emissions by combining two major emission methods: by burning fossil fuels and through the calcination of limestone (CaCO $_3$) [8]. During calcination limestone gets heated to produce lime (CaO while releasing substantial amounts of CO_2 to the atmosphere through the chemical reaction (CaCO $_3$ + heat \rightarrow CaO + $CO_2 \uparrow$). Each clinker production kilogram generates approximately 0.5 kg of CO_2 emissions according to research [9]. PC contains greater than 80% clinker so its manufacturing process produces massive CO_2 emissions automatically [10].

Annual global production of concrete amounts to 500 billion cubic yards which supports infrastructure development according to research [11-13]. Large-scale manufacturing of concrete made from Portland cement leads to more extensive CO₂ emissions in the global environment because PC represents a notable share of concrete construction. Finding environmentally friendly alternatives becomes essential because the industry requires materials which minimize cement production emissions without sacrificing construction performance standards.

The cement industry has validated MCs as concrete replacements through studies showing their natural capability for capturing atmospheric CO₂ [14]. The major component of these cements called magnesia (MgO) undergoes carbonation processes which transform carbon dioxide into stable magnesium carbonate molecules while maintaining well-established characteristics [14]. The construction sector has increasingly adopted MCs for emission reduction purposes to capture CO₂ effectively while enabling global carbon capture initiatives particularly during climate change times [15].

Different research works demonstrate numerous advantages MCs possess over PC. The useful properties of MCs extend to better mechanical performance and improved heat tolerance and increased CO₂ absorption potential and fireproof nature and the ability to assimilate industrial by-products while trapping harmful substances into their hydration products [16]. The production method of MgO through light-burnt MgO calcination at 600–1000°C together with hard-burnt MgO calcination at 1000–1400°C requires less CO₂ emissions and energy compared to the PC manufacturing process. Light-burnt MgO known as reactive magnesia holds potential to reduce CO₂ emissions substantially when applied to cement production because of its energy conservation properties [15].

The environmental advantages of MgO as a cement substance extend across manufacturing because this material shows potential for multiple cycles of usage [15]. Terrestrial dispersion of calcined MgO allows it to capture atmospheric CO_2 through crystal formation of magnesium carbonate. A circular manufacturing process would extract carbonate crystals to rebuild MgO and potentially eliminate up to 2–3 gigatons of CO_2 emissions annually which makes it an essential tool for climate change mitigation.

Scientists have explored carbonation extensively as a chemical process because it enables cementitious materials to react with atmospheric CCO₂ during their service life thus improving their mechanical properties and CO₂ storage potential. Previous studies show that carbonation curing severely influences the characteristics of pore spaces as well as hydration processes and material performance. Gruyaert et al. [12] discovered that carbon dioxide treatment modifies both the arrangement of void space and cement matrix's pore structure and chemical substance composition which results in enhanced materials strength while maintaining durability. Xuan et al. [13] combined with Zhang et al. [14] demonstrated that carbonation enhances both durability and mechanical properties of fiber-reinforced cementitious composites and recycled aggregate concrete.

Experienced growth as a tested method for capturing CO₂ within cement-based materials through accelerated carbonation curing (ACC) since recent years began. The carbonation process receives acceleration through ACC leading to greater CO₂ absorption efficiency for cement composites and improved hydration products as well as mortar and concrete microstructure integrity and early-age strength properties [15]. AC acceleration for carbonation offers better advantages than standard natural carbonation because it provides economical solutions and sustainable practices and technical implementability [16]. Modern research on accelerated carbonation technology investigated ACC as an element of magnesium cement (MC) composites to improve its potential for serving as an effective CO₂ storage solution.

The paper explores magnesium cement properties during carbonation reactions while studying how carbonation curing shapes their mechanical performance. Future research will concentrate on advancing both carbonated MC performance and on promoting their advancement as sustainable building

materials instead of traditional PC. The study aims to advance sustainable construction materials which support global climate change reduction through exploring the environmental and mechanical attributes of MCs.

CHARACTERISTICS OF MAGNESIUM CEMENTS AND THEIR CARBONATION REACTIONS

REACTIVE MAGNESIA CEMENT

Reactive magnesia cement (RMC) exists as a widely known binder system available both as an individual binder and as a modifying ingredient in Portland cement (PC). The material stands out because it shows potential to cut carbon dioxide emissions together with property strength enhancement. The addition of 2-3% RMC in PC production results in major enhancements of microstructural density alongside mechanical strength and durability. RMC provides dual protection against fire and corrosion as well as effective contaminant stabilization which turns it into an environmentally more beneficial substitute than traditional binders [17,18].

The main benefit of RMC involves its chemical CO₂ absorption process which also optimizes cement properties through Accelerated Carbonation Curing (ACC). The cement matrix absorbs CO₂ which dissolves into ions and generates natural and hydrated carbonate precipitates in its pore spaces during carbonation processes. The chemical reaction improves both material microstructure strength and establishes durable long-term properties [19]. RMC outperforms Portland cement because it has approximately 85% active MgO content which enables CO₂ absorption up to 92% while Portland cement reaches only 50.4% CO₂ absorption.

The ACC process involves a series of chemical reactions that lead to the formation of hydrated magnesium carbonates, which contribute to the increased strength and stability of RMC-based materials. These reactions occur as follows [20]:

$$MgO + CO_2 \rightarrow MgCO_3$$
 (Magnesite) (1)

$$MgO + H2O \rightarrow Mg(OH)_2$$
 (Brucite) (2)

$$Mg(OH)_2 + CO_2 + 2H_2O \rightarrow MgCO_3.3H_2O$$
 (Nesquehonite) (3)

$$2Mg(OH)_2 + CO_2 + 2H_2O \rightarrow Mg_2CO_3(OH)_2.3H_2O$$
 (Artinite) (4)

$$5Mg (OH)_2 + 4CO_2 \rightarrow Mg_5(CO_3)_4(OH)_2.4H_2O (Hydromagnesite)$$
 (5)

Brucite stands as the main hydration product when reactive magnesia cement (RMC) undergoes hydration. The combination of carbonation enables a significant increase in strength because it creates magnesium carbonate (MgCO $_3$) a durable mineral. Numerous carbonation products formed sequentially lead to denser material that generates a stable crystal network through their interconnection. The cement matrix receives additional strengthening power after the evolution of artinite into nesquehonite.

Increased carbonation conditions convert nesquehonite to dypingite according to Zarandi et al. [21] who studied the mineral phase evolution for structural strengthening. Carbonation products have been identified as strong components which enhance RMC density while building an effective interlocking mineral structure leading to better compressive strength and decreased porosity and superior environmental defense properties [22].

RMC requires minimal energy to manufacture because of which it produces greatly diminished carbon emissions during production when compared to conventional cement methods. RMC receives broad adoption in construction because it captures carbon dioxide effectively together with offering mechanical benefits for sustainable building applications. The schematic illustration in Figure 1 details the fundamental steps of magnesia carbonation along with their end products which demonstrate the reasons behind RMC's superior performance.

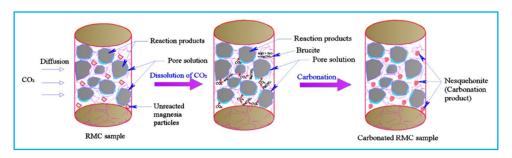


Figure 1. Carbonation mechanisms of magnesia (Source: [23])

Magnesium Phosphate/Potassium Cement

Due to its rapid setting capabilities MPC/MKPC cement obtains widespread use in performing quick repairs of roads and bridges and airport runways as well as other vital concrete structures to increase their instant strength capacity [24]. The emergency building sector finds this cement material beneficial because it reaches its peak strength quickly resulting in rapid reopening of repaired infrastructure.

The production of MPC takes place through the combination between deadburned magnesia (MgO) as an alkaline material and ammonium or potassium phosphate salts as acidic materials. Such reactions between acidic and basic components result in the formation of cementitious binders which demonstrate exceptional characteristics. MPC should not be grouped with conventional cement hydration because its dissolution-precipitation reaction forms stable phosphate-based compounds unlike normal cement that principally reacts with silicates and aluminates when coming into contact with water.

MPC finds use as a material of choice because it exhibits high early strength and quick setting time together with strong bond connections to ordinary concrete and low drying shrinkage rates and fire resistance [25]. MPC exhibits properties which suggest its usefulness as a material substitution for Portland cement (PC) in particular purposes including refractory applications and biomedical uses as

well as radioactive waste containment because it binds dangerous elements. The endurance properties of MPC work effectively in sulfate conditions and winter freezing conditions which increases its potential for structural repair across challenging environments.

The principal hydration product of MPC is struvite, a magnesium ammonium phosphate molecule, which formed by the following mechanism [26]:

$$MgO+KH_2PO_4$$
(potassium dihydrogen phosphate)+ $5H_2O \rightarrow MgKPO_4$. $6H_2O$ (K – struvite) (6)

$$MgO+NH_4H_2PO_4$$
 (ammonium dihydrogen phosphate) + $5H_2O \rightarrow MgNH_4PO_4$. $6H_2O$ (struvite) (7)

Magnesium Oxychloride Cement (MOC)

The production of magnesium oxychloride cement (MOC) occurs when MgO reacts with magnesium chloride (MgCl $_2$) solution in water to create a cement material with outstanding dry condition performance and strong resistance [27]. Strength development in MOC occurs independent of calcium-based components that function in Portland cement. The hydration process generates separate hydration phases which substantially affect MOC's physical properties and mechanical characteristics.

MOC properties related to hydration phases along with physical and mechanical aspects and microstructural features depend strongly on the solution concentration ratios between MgO and $\mathrm{MgCl_2}$. MOC strength and fire resistance along with compressive strength and flexural strength increase when the solution ratios are properly optimized. Manufacturers extensively use MOC because it sets rapidly for numerous industrial applications like flooring systems and fireproofing materials together with prefabricated construction elements. The exceptional microstructure of MOC delivers enhanced thermal insulation which qualifies the material for building projects requiring extreme temperature tolerance.

At room temperature, the development of hydration phases in MOC can be described by the following chemical reactions [28]:

$$5MgO + MgCl_2 + 13H_2O = 5Mg(OH)_2$$
, $MgCl_2$, $8H_2O$ (Phase 5) (8)

$$3MgO + MgCl_2 + 11H_2O = 3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O \text{ (Phase 3)}$$
 (9)

The rigid and strong characteristics of MOC are mainly delivered through two predominant crystalline hydration phases known as Phase 5 and Phase 3. The mechanical properties of MOC composites remain impressive in dry environments yet these properties substantially decrease when the material is submerged in water environments [29]. Wet conditions cause breakdown of cement materials because the essential water-containing mineral phases Phase 5 and Phase 3 dissolve after contact with water [28]. The sensitivity to water exposure restricts MOC applications outdoors unless protective measures are implemented or modifications made to boost its resistance against water decline.

Scientists have recently tried different methods to enhance MOC water resistance including the addition of nanoparticles together with polymers and supplementary cementitious materials to strengthen the hydration phases. The recent findings seek to expand MOC usage in construction without compromising its established properties of strength and fire-resistance and sustainability aspects. Researchers behind future studies work on developing inventive formulations to make MOC less sensitive to moisture so it can gain broader cement industry applications.

MAGNESIUM OXYSULFATE CEMENT

MOS cement develops through chemical processes between refined MgO and MgSO₄·7H₂O solutions (magnesium sulfate) in a manner comparable to MOC production [30]. MOS cement stands out as a friendly cementive material because its manufacturing process consumes less energy and avoids requiring high-temperature calcination stages [31,32]. The sustainable construction sector uses MOS as a low-carbon alternative material because it performs better than standard cementitious materials.

Scientific research established that the hydration produces $5 \text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ which the scientific community identifies as the $5 \cdot 1 \cdot 7$ phase responsible for strengthening and stabilizing MOS matrices [33]. Various researchers have established that MOS hydration products contain multiple compounds which can be expressed through the generalized formula $\text{xMg}(\text{OH})_2 \cdot \text{yMgSO}_4 \cdot \text{zH}_2\text{O}$ beyond the $5 \cdot 1 \cdot 7$ phase [34]. The main hydration processes leading to MOS development occur through the following series of reactions:

$$3MgO + MgSO_4 + 11H_2O \rightarrow 3Mg(OH)_2$$
. $MgSO_4$. $8H_2O$ (Phase $3 - 1 - 8$) (10)

$$5MgO + MgSO_4 + 7H_2O \rightarrow 5Mg(OH)_2$$
. $MgSO_4$. $2H_2O$ (Phase 5 – 1 – 2 or 3) (11)

The creation of these phases serves as the fundamental determinant for establishing the mechanical attributes of MOS-based materials. MOS demonstrates high resistance to heat while maintaining low shrinkage and sufficient mechanical strength as it proves suitable for multiple applications which include construction elements and fire-resistant boards.

The durability of MOS matrices receives additional benefit from carbonation curing which results from early CO_2 sequestration leading to immediate mechanical strength increase. The microstructure densification through this method results in better material compactness while decreasing amounts of capillary pores. The long-term carbonation process leads to structural degradation because excess carbonate products transform cement binding stages [30]. The studies by Ba et al. [35] demonstrated that carbonation cure of MOS produces MgCO_3 structures through the neutralization of MgSO_4 and $\mathrm{Mg(OH)}_2$ phases which ultimately enhances both compactness and mechanical resistance to a particular threshold [33]. The carbonation reaction involving MOS adopts this formula [30]:

$$(n+1)Mg(OH)_2 \cdot MgSO_4 \cdot (m+1)H_2O + CO_2 \rightarrow MgCO_3 + nMg(OH)_2 \cdot MgSO_4 \cdot mH_2O$$
(12)

Recent advancements in MOS research have focused on optimizing its composition to maximize durability while mitigating its susceptibility to long-term carbonation effects. The development of composite MOS materials incorporating supplementary binders and nano-modifications has further expanded its potential applications in sustainable and resilient infrastructure.

Influence of carbonation curing on MCs properties Mechanical Strength

The strength characteristics of magnesium cements under the impact of ACC are thoroughly evaluated through the research findings presented in Tables 1. The use of ACC produced an 83% rise in compressive strength (CS) while testing against normal control specimens that were not supplemented with ACC according to Pu and Unluer [36]. The quick formation of stable carbonation products during synthesis creates a denser microstructure and improves durability because of which strength values increase strongly. The carbon saturation value measurements of RMC samples increased consistently with the amount of CO₂ captured according to Jang et al. [37]. The development of hydromagnesite carbonates (Mg5(CO₃)4(OH)₂·0.4H₂O) as the primary responsible factor for increasing CS contributed to enhancing microstructure density and mechanical performance by filling the inner voids of porous structures. Strength test data from carbonated MPC matrices shows superior results compared to matrices prepared with control method approaches according to Table 1. Jeon et al. [38] documented MPC specimens healed with CO₂ reaching superior compressive strength (CS) as well as strain at peak stress in comparison with regular air curing. Laboratory tests showed that carbonated material strength increased because CO₂ produced denser surroundings around dead-burned magnesia hydration products. Internal material porosity becomes minimized through this densification process to create a solid and durable structure. The research by Gao et al. [39] revealed that MPC materials containing fly ash gained equivalent strength rates after ACC compared to standard MPC samples without carbonation treatment. The combination of fly ash served two functions: first it activated the pozzolanic reaction then it generated new carbonated phases which strengthened the composite material and extended its durability.

Table 1 shows that MOC and MOS composite specimens possess different strengths between carbonated and non-carbonated conditions. The MOC paste containing powdered fuel ash (PFA) under CO_2 curing treatment exhibited enhanced strength performance and water resistance according to He et al. [29]. The increased performance of the material stemmed from additional carbonated phases forming thus strengthening the matrix structure and making it more resistant to damp environments. The authors of Ba et al. [35] established that MOS samples experiences increased strength and toughness under carbonation curing conditions because this process reduces the water-to-cement ratio and refines mesopores. The material acquired higher mechanical strength and better environmental protection from degradation because mesoporosity diminished to

create a denser structure. Zhang et al. [30] discovered analogous findings which explain how MOS hydration products can interact with CO_2 substances to form new crystals for ultimate strength enhancement. The conversion of hydration phases into durable carbonated compounds through this process significantly enhances material bearing strength and durability which makes the material suitable for architectural applications.

Table 1. Influence of ACC on strength properties of RMC, MPC, MOS and MOC composites

Ref.	Raw materials and mix proportions	ACC Conditions	Testing Age	Compressive Strength (CS) (MPa)		Flexular Strength (FS) (MPa)				
				control	in ACC	control	in ACC			
RMC										
Jang et	-RMC burned with	- 25°C	28d	0.7	2.4	-	-			
al. [37]	700°C, 80%	- RH2 95%								
	-Hydrated magnesium	- CO ₂ concentration								
	carbonate, 20%	0.03%								
Wang et	-RMC paste	-RH 98%	7d	23	83	-	-			
al. [40}	-W/C=0.25	- CO2 concentration								
	-H2SO4(0.125wt% of	100%								
	paste)									
	-HNO3(0.0137wt % of									
	paste)									
Hay and	-RMC	-30 °C	28	6	23	-	-			
Celik	-W/C=0.55	-RH 80%								
[41]		-20% CO ₂								
Pu and	-RMC (10%)	- 30 2 °C	7	-	25	-	-			
Unluer	-Aggregates (90%)	- RH 80 + 5%								
[36]	-W/C = 0.70	- 10% CO ₂								
MPC										
Jeon et	-DBM/KDP = 4 (MR)	-20 °C,	28d	29.0	38.6	-	-			
al. [38]	W/C = 0.45	- RH 60%								
	-Borax 5%	- CO2 concentration								
	-A/B 4	of 20%								
		-Atmospheric pressure								
Yuxin et	-DBM/ADP = 3 (Wt. %	-20 + 5°C.	35d	36.5	39.4	10.2	12.9			
al. [39]	-Borax 6%	-RH 70 + 5%								
	-W/C = 0.12	- CO2 concentration								
	-Fly ash = 14%	20 + 3%								

Table 1. Continued

Ref.	Raw materials and mix proportions	ACC Conditions	Testing Age	Compressive Strength (CS) (MPa)		Flexular Strength (FS) (MPa)					
				control	in ACC	control	in ACC				
МОС											
He et al.	- MgO/MgCl ₂ =9	-25°C	28	130	170	-	-				
[29]	- H ₂ O/MgCl ₂ =16	-RH 55%									
		-> 99% CO ₂									
MOS											
Ba et al.	-RMC	-20 +5 °C	28+ 7 d	51.0	53.0	4.8	5.0				
[35]	-MS (MgSO ₄ .7HO)	-RH 70 5 %									
	-RMC/MS= 2.28	- 20% CO ₂									
	-W/C=0.35										
Zhang	-MgO/ MgSO ₄ 7H ₂ O/	-20 °C22°C	28 + 28	114	119	-	-				
et al.	H ₂ O=8:1:12	-60% +5% RH									
[30]		- 20% CO ₂									
Li et al.	-MgO:	- 20 °C	28	78	82	22	25				
[32]	4.7H ₂ O:H ₂ O=21:1:12	- 60% RH									
	- Citric acid 0.5%	- 20% CO ₂									
		_									
Hu et al.	- MgO: MgSO ₄ .7H ₂ O:	-25 + 2 °C	28	81	84	-	_				
[42]	H ₂ O=2:1:1	-60 + 5% RH									
	- Citric acid 0.5%	-0.5 MPa CO ₂									

CONCLUSION

The engineering sector views MCs as a prospective substitution for PC cement because they reduce carbon emissions while providing better mechanical strength and perform enhanced CO_2 burial functions. Four types of magnesium cements known as Reactive Magnesia Cement (RMC), Magnesium Phosphate Cement (MPC) and Magnesium Oxychloride Cement (MOC) and Magnesium Oxysulfate Cement (MOS) show distinct beneficial characteristics that include fast setting times and high early strength performance and fire resistance along with durability. ACC optimized the sustainability through carbonization reactions that produced stable carbonates which reduced total CO_2 emissions.

The deployment of MCs suffers from three main limitations which include water sensitivity and restricted scalable use and expensive production. The practical implementation of Microbial Cements depends on solving multiple problems through improved manufacturing processes as well as material development and hybrid cement technology. Research in the future needs to tackle the water sensitivity of MCs while developing large-scale production technologies and integrating industrial debris into MC development to create budget-friendly green construction materials.

Future advancements in MC production will transform sustainable construction because they present a feasible approach to developing carbon-

neutral building materials. These storage capabilities make them vital elements in cutting climate change effects while maintaining their structural properties and overall performance.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

AUTHOR CONTRIBUTIONS

Md. Saniul Haque Mahi: writing - original draft, resources. Md. Hasibul Khan: conceptualization, supervision. Abhijit Nath Abhi: conceptualization, supervision. Md. Foysal Sheik: visualisation. Md. Kamal Hossen: formal analysis.

DATA AVAILABILITY STATEMENT

The data used to support the findings of this study are included within the article.

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