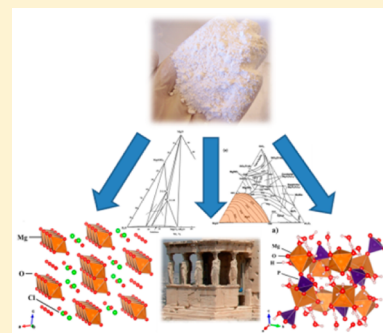


Magnesia-Based Cements: A Journey of 150 Years, and Cements for the Future?

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ABSTRACT: This review examines the detailed chemical insights that have been generated through 150 years of work worldwide on magnesium-based inorganic cements, with a focus on both scientific and patent literature. Magnesium carbonate, phosphate, silicate-hydrate, and oxysalt (both chloride and sulfate) cements are all assessed. Many such cements are ideally suited to specialist applications in precast construction, road repair, and other fields including nuclear waste immobilization. The majority of MgO-based cements are more costly to produce than Portland cement because of the relatively high cost of reactive sources of MgO and do not have a sufficiently high internal pH to passivate mild steel reinforcing bars. This precludes MgO-based cements from providing a large-scale replacement for Portland cement in the production of steel-reinforced concretes for civil engineering applications, despite the potential for CO₂ emissions reductions offered by some such systems. Nonetheless, in uses that do not require steel reinforcement, and in locations where the MgO can be sourced at a competitive price, a detailed understanding of these systems enables their specification, design, and selection as advanced engineering materials with a strongly defined chemical basis.



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1. INTRODUCTION

1.1. Cements Based on MgO

The statement “everything old is new again” is certainly relevant to the current status of cements based on magnesium (MgO). The global construction materials industry, which was historically based on an extremely wide range of materials suitable for local conditions and specific applications, moved through the latter half of the 20th century to become almost a monoculture based on the use of Portland cement (PC), with other materials essentially sidelined. With the push for increasing environmental sustainability in the construction industry in the 21st century, we are now facing a situation where the global industry is rediscovering large-scale interest in materials that, for decades, held largely niche or curiosity value. This has led to the reinvention of a large quantity of information that was previously more widely understood. The key purpose of this review is to bring this information to light in the context of the modern use of MgO-based cements, integrated with results generated more recently as these materials have come back into focus and utilization. In particular, this synthesis of information demonstrates the value of high-quality chemical and analytical data in designing and specifying these materials.

The dominant form of cement used worldwide is Portland cement, with approximately 4 billion tonnes produced in 2014.¹ Named in the 19th century because of its apparent visual resemblance to limestone quarried from the Isle of Portland, U.K., this cement consists primarily of hydraulic calcium silicate phases, which are produced in a kiln at elevated temperature to produce “clinker”, which is then cooled and interground with gypsum. The resulting powder is a hydraulic cement that will hydrate when combined with water, forming a cohesive, strong, and dimensionally stable monolith. Hydrated PC has a high internal pH, generally around 12–13, that holds embedded mild steel reinforcing in a passive state, offering some degree of protection from the corrosive action of aggressive agents such as chlorides.² In typical usage, PC is blended with sand to form a mortar, or with fine and coarse aggregate to form a concrete, and can also be blended with a variety of “supplementary cementitious materials”, including coal fly ash, blast-furnace slag, and other finely divided silicate and aluminosilicate powders, to enhance technical properties, cost, and/or environmental credentials. There is however an ongoing search for alternatives to PC because of its large CO₂ emissions footprint,³ which comprises around 8% of global anthropogenic greenhouse-gas emissions at present.⁴ One class of materials that has been identified as a potential low-CO₂ alternative to PC and has actually been used in industrial practice for more than 150 years is the broad group of MgO-based cements that form the subject of this review.

In recent decades, the major motivation for the development and uptake of MgO-based cements has been driven from an environmental standpoint. The lower temperatures required for the production of MgO compared to the conversion of CaCO₃ to PC and the energy savings associated with this reduced temperature have led many to envision MgO-based cements as being central to the future of ecofriendly cement production. Equally, the ability of MgO to absorb CO₂ from the atmosphere to form a range of carbonates and hydroxycarbonates lends itself well to the discussion of “carbon-neutral” cements, which could potentially absorb close to as much CO₂ during their service life as was emitted during their

manufacture. These two interconnected aspects have led to a recent explosion in interest, both academic and commercial, in the area of MgO-based cements.

In the past, MgO-based cements were seen as a way to utilize abundant local resources or to achieve perceived commercial advantages over PC such as desirable aesthetic or mechanical properties. Much impetus has come from workers in locations close to, or companies involved with, magnesium-rich brines such as those of the Great Salt Lake (Utah), the Chinese salt lakes (Qinghai, Xinjiang, and Tibet), and the Dead Sea (Israel/Jordan). However, this geological concentration of magnesium within certain brines and geological formations, which has attracted entrepreneurs and scientists, could prove to be the Achilles heel of magnesium cements in a global sense. Calcination of magnesite (MgCO₃) is the principal route by which MgO is obtained for use as a raw material in these cements, but reserves of magnesite are geographically limited, with large-scale deposits found in only a handful of countries. In Europe, magnesite is sufficiently scarce and in-demand that it was listed on the 2014 EU “Critical Raw Materials” list,⁵ even without large-scale production of MgO-based cements in that region at present. China, North Korea, and Russia account for >65% of global declared reserves,⁶ with China being the largest magnesite producer. MgO production can also occur close to saline lakes (themselves geographically limited) or through precipitation as Mg(OH)₂ from seawater, although the latter option is considered energy-intensive unless the brine is already highly concentrated, such as in a desalination operation.

Magnesia-based cements, by definition, use MgO as a building block rather than the CaO that comprises more than 60% of the elemental composition of PC. Because of the substantially different chemistry of MgO compared to that of CaO, one cannot simply change the feedstock for conventional Ca-based cements to produce a directly corresponding material using the same infrastructure. Comparison of the respective (MgO,CaO)–Al₂O₃–SiO₂ ternary phase diagrams (Figure 1) shows vast differences in chemistry and phase formation. Specifically, no magnesium silicate phases are formed at elevated temperatures that have hydraulic properties akin to those formed in the calcium-rich region of the CaO–SiO₂–Al₂O₃ system: Ca₃SiO₅, Ca₂SiO₄, and Ca₃Al₂O₆ (shaded regions in Figure 1b) are key hydraulic phases in PC, but have no magnesian analogues in Figure 1a.

This therefore precludes the direct replacement of CaO in PC manufacture with MgO, and therefore, different approaches are required for the development and utilization of MgO-based cements. Some of the possible approaches that have been demonstrated include the combination of carbonates or other oxysalts with MgO to form a solid cohesive mineral gel or mass (a “binder” in cement terminology) and also the production of acid–base cements through the reaction between MgO and acid phosphates. This review discusses each of these subclasses of magnesium-based cements in turn, with a particular focus on understanding the links between the chemistry and applications of each available class of materials.

1.2. Magnesia Production

Commercially produced magnesium oxide (commonly referred to as magnesia or periclase) is not mined directly, as periclase itself is relatively rare in nature and its hydration product brucite [Mg(OH)₂] occurs in only a limited number of commercially viable geological formations. MgO is instead generally obtained either by a dry route from the calcination of

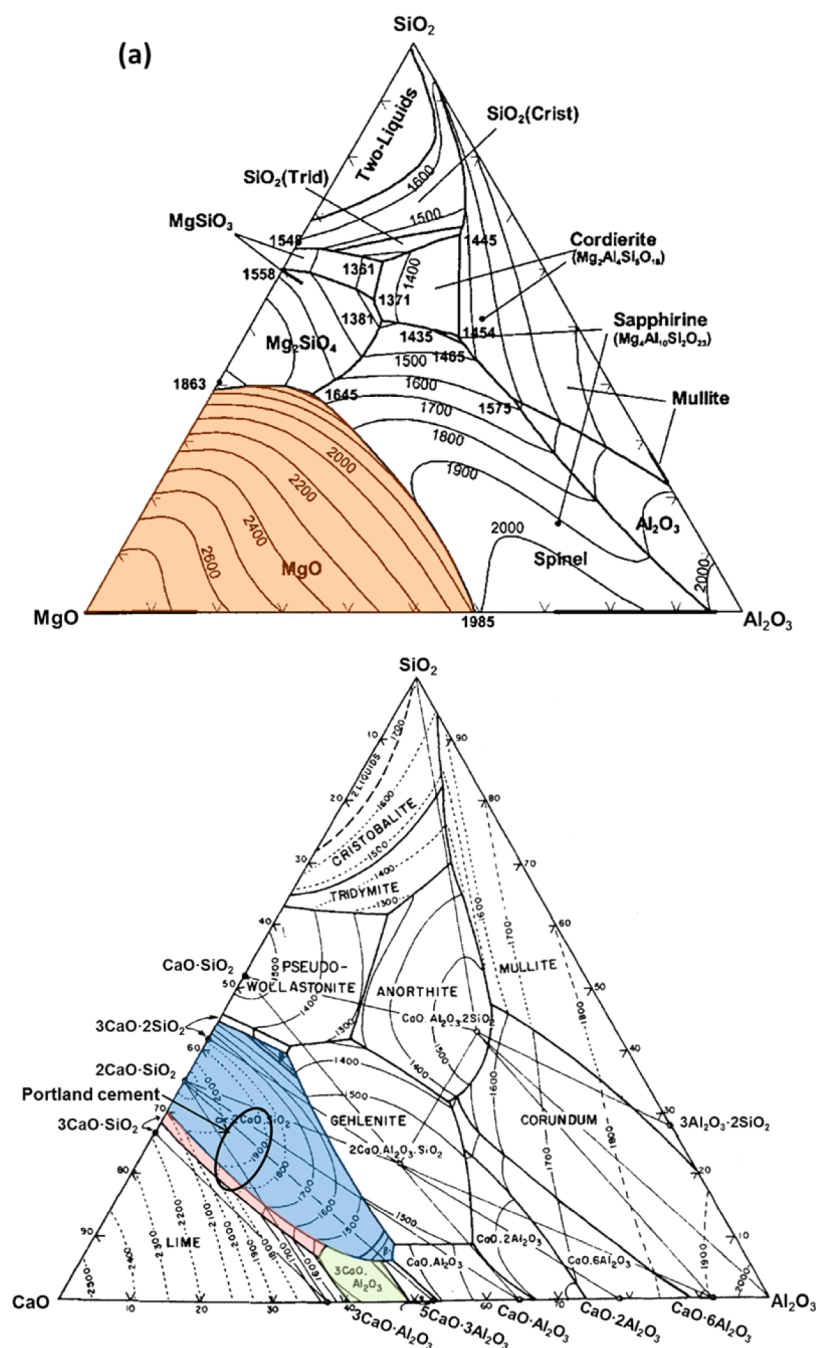
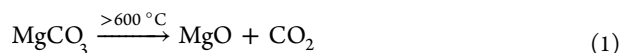


Figure 1. Ternary phase diagrams, in units of weight percent, for the systems (a) MgO–SiO₂–Al₂O₃ and (b) CaO–SiO₂–Al₂O₃. Adapted from refs 7 and 8.

mined magnesite deposits (MgCO₃) or by a wet route from solutions of magnesium-bearing brines or seawater. The bulk of MgO production worldwide is achieved through calcination of magnesite because of the higher energy requirements for production through the wet route.^{9,10}

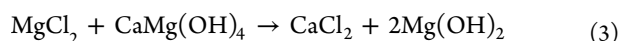
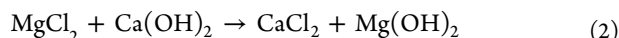
The dry route for MgO production typically requires the crushing of magnesite before calcination through the process



Higher-grade MgO requires careful selection of MgCO₃-bearing rocks or pretreatment due to Fe₂O₃ and SiO₂ impurities, which can adversely affect the refractory usage of MgO.¹¹

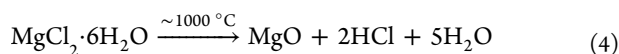
The wet route is more complex in chemical terms, but it normally requires the precipitation of Mg(OH)₂ from a solution rich in magnesium, typically solution-mining brines or (more dilute) seawater. The former is exemplified at Veendam, The Netherlands, where water is injected into a MgCl₂-rich salt formation and returned to the surface under hydrostatic pressure. Although varying from region to region, seawater contains an average Mg concentration of ~1.29–1.35 g/L,^{12,13} thus constituting a vast resource of magnesium. The concentrated brines or seawaters can be deborated through ion-exchange resins, and the sulfate concentrations can be reduced through the addition of CaCl₂ brines to precipitate CaSO₄·2H₂O and yield a purified MgCl₂-rich brine.^{14,15} This is then reacted with slaked lime or dolime [Ca(OH)₂ or CaMg(OH)₄],

obtained by calcination followed by hydration of limestone or dolomite, respectively] to precipitate $\text{Mg}(\text{OH})_2$, according to the equations



The resultant $\text{Mg}(\text{OH})_2$ slurry is then filtered, washed, and calcined to form MgO . This material can be briquetted and then further sintered, if required.^{16,17}

The wet route can also occur through the pyrohydrolysis of magnesium chlorides in superheated steam up to 1000 °C.^{15,17} A current commercial-scale example is the Aman spray roasting process,^{17,18} described by



MgO produced by either the dry or wet route can be further calcined at varying temperatures depending on the end purpose. Increasing the residence time within calciners and increasing the temperature reduce the MgO surface area, increase the crystallite size, and reduce the reactivity as a result of sintering.^{11,19–22} This enables a range of MgO products to be produced depending on the degree of reactivity required. MgO is typically labeled by calcination temperature, which has resulted in varying overlapping definitions. The European Commission has defined grades of MgO as follows:⁹

- caustic-calcined, 600–1300 °C;
- dead-burned, 1600–2200 °C; and
- fused, >2800 °C.

In contrast, a producer of MgO ,²³ in common with much of the technical literature, uses the grades

- light-burned, 700–1000 °C;
- hard-burned, 1000–1500 °C; and
- dead-burned, 1500–2000 °C.

Dead-burned MgO is typically used in the refractories industry to form linings and bricks, principally because of its high melting point. Caustic-calcined/light-burned MgO finds a range of applications in agriculture, the paper and pharmaceuticals industries, fire proofing, and many more.^{9,15} The reactivity of MgO tends to decrease with increasing processing temperature, and MgO processed at the lower end of the light-burned range is also described, particularly within the cements community, as “reactive magnesia”; see section 2.1.

The determination and optimization of the reactivity of MgO for cement applications has been the subject of much discussion, and a variety of tests are used to determine MgO reactivity. These include the time taken to neutralize an organic acid and surface area as determined by gas sorption, iodine adsorption, and other techniques.^{10,24–26} The effects of variations in reactivity due to calcination conditions and MgO impurities are further discussed below in relation to the respective magnesium cements presented in this review, as much of the research pertains to the optimization of chemical reaction processes taking place in specific cements.

2. MAGNESIUM CARBONATE AND REACTIVE MAGNESIA CEMENTS

Magnesium carbonate and reactive magnesia (MgO) cements have gained significant popularity over the past decade, largely because of concerns over climate change and, in particular, the intention and need to mitigate the CO_2 emissions associated

with conventional PC manufacture. Magnesium can form a wide range of carbonates and hydroxycarbonates (Table 1),

Table 1. Magnesium Minerals Identified in MgO Cements

mineral	composition	density (g/cm^3)
brucite	$\text{Mg}(\text{OH})_2$	2.38, ref 30
magnesite	MgCO_3	3.01, ref 31
nesquehonite	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	1.85, ref 32
lansfordite	$\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$	1.70, ref 33
artinite	$\text{Mg}_2(\text{CO}_3)(\text{OH})_2 \cdot 3\text{H}_2\text{O}$	2.03, ref 34
hydromagnesite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	2.25, ref 35
dypingite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$	2.15, ref 36
huntite	$\text{CaMg}_3(\text{CO}_3)_4$	2.70, ref 37

leading some to propose that it is possible to develop large-scale production of cements with reduced CO_2 emissions, or even “ CO_2 -negative” cements, by the uptake of atmospheric CO_2 to form such products.^{27–29} Carbonation of MgO can be described in general as the formation of magnesite from MgO through the uptake of carbon dioxide as in

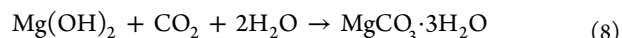
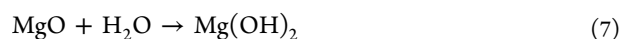


or through the incorporation of water to form nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) as in



2.1. Reactive Magnesia

The materials described in the technical literature as reactive magnesia cements often involve the addition of fine reactive MgO to conventional PC systems, resulting in the formation of $\text{Mg}(\text{OH})_2$, and subsequent carbonation to a hydrated magnesium carbonate, as exemplified for the case of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ in the equations



This cementing system has been envisaged to replace either a large fraction or the majority of PC in a binder system, thus resulting in a lower carbon footprint for the cement as a whole. However, regulatory standards currently place tight restrictions on the MgO content of PC-based cements because of the long-term dimensional instability experienced when MgO grains are present within PC; see section 2.2.

2.2. Expansive MgO Cements

It should be noted that the materials described as reactive MgO cements are quite distinct from the use of smaller quantities of reactive MgO as an expansive additive in cement binders, often in dam construction and other large civil engineering projects, particularly in China, to compensate for the slight natural shrinkage of PC during hydration, which can continue for months or years in service.^{38,39} The emplacement of large cement/concrete monoliths presents challenges associated with cooling shrinkage of cement paste after hardening, although this is lessened by the use of special low-heat cements or extensive use of supplementary cementitious materials. This is due to the highly exothermic nature of cement hydration, which can release up to 500 J per gram of cement. Hydration of the cement in such large volumes of concrete can result in temperature rises in excess of 50 °C, extending long after the

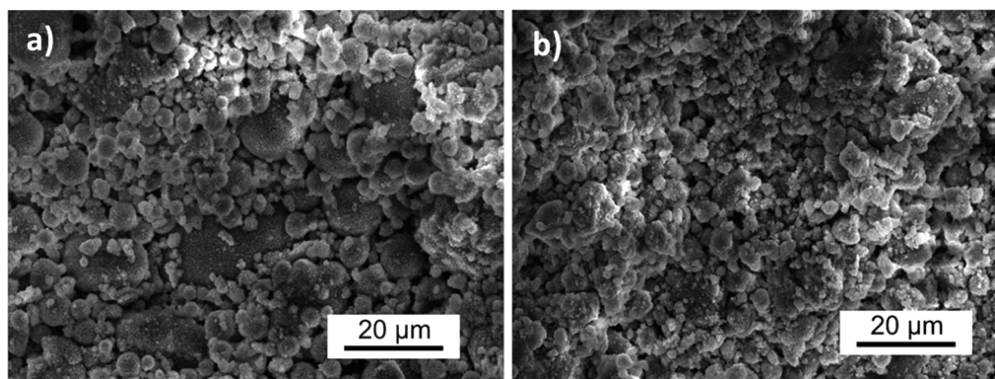


Figure 2. Secondary electron micrographs of MgO/FA binders after 14 days of curing under ambient conditions with varying compositions of MgO/FA = (a) 10:90 and (b) 50:50, showing little development of a cohesive binding phase in either case. Reproduced with permission from ref 62. Copyright 2008 Elsevier Ltd.

concrete has hardened, up to 6 months after pouring.^{40–42} As the concrete cools, it contracts, leaving a dam liable to cracking.

Shrinkage-compensating and expansive cements have long been used for various civil engineering projects.^{41,43,44} These are typically based on increasing the aluminate and sulfate concentrations of cements by adding ye'elimite ($\text{Ca}_4\text{Al}_6\text{O}_{12}\text{SO}_4$) and anhydrite (CaSO_4), forming expansive ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$] crystals upon hydration.^{39,43–45} Recently, cements based on ye'elimite, dicalcium silicate, and calcium ferrite phases^{46,47} have gained interest, with the degree of expansion controlled by water content in the mix. These cements are typically used where it is essential that the cracks do not form upon autogenous or drying shrinkage, such as in water towers, pipes, and runways.⁴⁸

In large structural applications, however, where shrinkage is often observed as a result of cooling after an initial exothermic hydration reaction rather than autogenous or drying shrinkage of the cement hydrates, conventional shrinkage-compensating cements are unsuitable, as shrinkage occurs long after the desired expansive products have formed. For this purpose, MgO expansive cements have been gaining momentum. These rely on the expansive hydration of MgO to $\text{Mg}(\text{OH})_2$, resulting in a 117% molar solid volume expansion.⁴⁹ The use of MgO requires careful calcination and control of fineness and dosage to ensure that expansion is delayed to occur during cooling, but not so delayed as to cause long-term dimensional stability issues within these cements.^{50–53} Further details about these expansive MgO-containing cements are provided in a concise review by Du³⁸ and a recent comprehensive review by Mo et al.⁵⁴

2.3. Development of Reactive Magnesia Cements

In recent years, there has been considerable interest in reactive magnesia (MgO) cements containing a very high content of MgO, although much of the work has appeared in the patent literature or online sources rather than in peer-reviewed publications.^{55–59} It has been claimed that reactive magnesium cements can be carbon-negative⁶⁰ when a carbon-recycling cement kiln is used in the production of the reactive MgO and when also considering the later CO_2 uptake by the cement in service. The U.S. patent awarded to Harrison of the Australian company TecEco, based on a 2001 submission,⁵⁶ describes the use of extended curing durations and sometimes steam curing to produce strong blocks based on blends of MgO, a pozzolan, and PC. The MgO used is produced by calcination of MgCO_3 at a relatively low temperature, $\sim 650^\circ\text{C}$, which induces lattice

strain and porosity in the MgO particles that would be annealed out if processed at higher temperatures.¹¹ This enables control of the reactivity of the MgO according to the treatment conditions and particle size, to ensure that it hydrates at the same time as the other cementitious components, and is thus defined as “reactive”. Importantly, this MgO reacts much more rapidly than dead-burned sources of MgO (low-reactivity MgO calcined at $>1500^\circ\text{C}$), such as the free MgO in Portland clinker, which are fired at much higher temperatures and thus typically hydrate slowly, causing cracking within conventional cements as an expansive chemical reaction is induced locally within a material that has already hardened.⁶¹

It is also claimed⁵⁶ that the addition of ferrous sulfate can improve the durability and strength of reactive MgO cements. This is likely to be due to the formation of magnesium oxysulfate phases (cf. section 6.1) during steam curing, in parallel with $\text{Mg}(\text{OH})_2$.

This line of inquiry was further developed by Vandeperre et al.^{62,63} who studied the hydration and microstructure of cements made from coal fly ash (FA) with the addition of up to 50 wt % (MgO + PC) and confirmed that the addition of reactive MgO does not induce the delayed expansive cracking normally associated with less-reactive MgO in PC systems. However, lower compressive strengths were observed when MgO was added because of the lower PC content in these mixes, as well as higher water demand and higher porosity. For example, one formulation using commercial superfine reactive (“XLM”) MgO and FA with the formulation FA/PC/MgO = 50:50:0 achieved an unconfined compressive strength of 34 MPa. Replacing half of the PC with MgO (50:25:25) gave a strength of 20 MPa, and further reducing the PC content (50:10:40) yielded a strength of only 8.5 MPa,⁶³ rendering this cement less useful as a structural binder. For comparison, common European cements are required to achieve minimum compressive strengths between 32.5 and 52.5 MPa after 28 days, depending on the grade specified.⁶⁴ The MgO was observed to hydrate to form $\text{Mg}(\text{OH})_2$ alone, with no magnesium carbonate phases detected, resulting in a poorly connected microstructure, as shown in Figure 2. Furthermore, the MgO was observed to have no influence on the PC hydrate phases formed at up to 35 days of hydration.⁶³ This study confirmed that, at least during the first month of curing, these reactive MgO–PC-blended cements do not take up a measurable quantity of environmental CO_2 and are thus unlikely to be carbon-negative, or even carbon-neutral, in the

short to intermediate term. Cwirzen and Habermehl-Cwirzen⁶⁵ also observed that the freeze–thaw resistance and flexural and compressive strengths were reduced because of increased capillary porosity when MgO is added to a PC-based system.

The application of accelerated-carbonation curing conditions to reactive MgO systems, however, provided a very different outcome. MgO/PC/FA- and MgO/FA-based cements were air cured for 14 days at 98% relative humidity (RH), before being cut into 5-mm-thick samples. These samples were then cured for a further 28 days either in air at 98% RH as a control or under accelerated-carbonation conditions using controlled CO₂ atmospheres at ambient pressure containing 5% or 20% CO₂ by volume, at 65% or 95% RH.⁶⁶ Under atmospheric CO₂ conditions, neither of these systems formed magnesium carbonates; however, under accelerated-carbonation conditions MgCO₃·3H₂O formed in both systems (Table 2), along with calcite, CaCO₃, resulting from the carbonation of PC hydration and pozzolanic FA reaction products.

Table 2. Key Phases Identified by XRD in FA/PC/MgO Samples after 21 Days of Curing in Controlled CO₂ Environments at Ambient Pressure^{66 a}

FA/PC/MgO sample (wt %)	RH (%)	CO ₂ (vol %)	Mg(OH) ₂	MgCO ₃ ·3H ₂ O	CaCO ₃
90:0:10	98	0.04	X	—	—
		20	—	X	X
	65	20	X	—	minor
90:5:5	98	0.04	X	—	X
		20	—	X	X
	65	20	—	—	X
50:0:50	98	0.04	X	—	minor
		5	X	X	X
		20	X	X	X
	65	5	X	—	X
		20	X	X	X
50:25:25	98	0.04	X	—	X
		5	X	X	X
		20	X	X	X
	65	5	X	—	X
		20	X	—	X

^aX denotes presence of the phase, whereas a dash (—) denotes its absence.

The ability to form identifiable quantities of the carbonated magnesium phase MgCO₃·3H₂O is evidently controlled by a combination of MgO content, relative humidity, and CO₂ concentration. In the lower MgO samples containing 90% FA, MgCO₃·3H₂O was formed only at 98% RH and 20% CO₂. This does show the potential for forming both PC-free and PC containing low-binder materials that can then be carbonated, however. The samples containing 50% FA were more amenable to carbonation, with the PC-free system (50:0:50) producing readily identifiable amounts of MgCO₃·3H₂O at both 5% and 20% CO₂ and 98% RH, although 20% CO₂ was required in a lower-humidity environment (65% RH). The addition of PC to this system reduced the carbonation of MgO, requiring a 98% RH environment to form MgCO₃·3H₂O, although this was achieved with CO₂ concentrations of both 5% and 20%. This demonstrates that carbonation of these reactive MgO cements is possible, when formulated both PC-free and containing PC; however, greatly increased levels of CO₂ are required during curing, and control of humidity is paramount.

The PC-free system (MgO/FA) showed a significant increase in fracture toughness in three-point bending geometry following accelerated carbonation when compared to the low values of toughness obtained under natural curing conditions, whereas the physical properties of the MgO/PC/FA systems appeared unaffected by carbonation.⁶⁶ It must be noted, however, that these samples were thin plates (5 mm thick) and were therefore much more amenable to accelerated carbonation than units with greater wall thicknesses such as blocks because of limitations on the diffusion rate of CO₂ into a thicker element.

Unfortunately, there have been no published long-term studies of reactive MgO cements, meaning that the durability performance of these materials is difficult to validate. Specifically, it is unclear whether the Mg(OH)₂ formed within the MgO/PC systems will actually undergo the postulated carbonation processes over a time frame of several years under conditions of natural atmospheric exposure. If not, this calls into question the overall environmental advantages of reactive MgO cements without the implementation of accelerated carbonation.

Recently, studies on reactive MgO were undertaken by Mo and Panesar, who focused on the accelerated carbonation of MgO/PC blends with and without addition of ground granulated blast-furnace slag (BFS).^{67–69} These cements contained up to 40 wt % MgO, with the major carbonate phases formed being MgCO₃·3H₂O and CaCO₃ (both calcite and aragonite polymorphs). These studies employed rather extreme carbonation conditions for cements: Samples were vacuum-dried to remove capillary moisture, before being exposed to a 99.9% CO₂, 98% RH atmosphere, enabling rapid carbonation of the specimens. It was claimed that the presence of MgO altered the calcite formation, resulting in the formation of a magnesian calcite, which, along with the deposition of MgCO₃·3H₂O, reduced sample porosity, densifying the microstructure and increasing the microhardness. Because of the relatively extreme carbonation conditions, it remains to be seen whether this carbonation regime could be employed on a commercial scale or is viable in larger products.

There remains open discussion about the role of Mg during the formation of calcite in the carbonation of MgO-containing PC systems. Although the formation of magnesian calcite has been claimed by Mo and Panesar,^{64–66} the work of Vandeperre et al.^{62,66} did not indicate the incorporation of Mg within calcite during atmospheric or mildly accelerated carbonation of reactive MgO cements. The effects of the Mg/Ca ratio on the formation of calcite and related CaCO₃ polymorphs (vaterite and aragonite) are the subject of an extensive literature with regard to seawater: Increasing Mg/Ca ratios are known to influence aragonite formation instead of calcite in seawater, and magnesian calcites can precipitate from Mg-enriched seawaters and chloride solutions.^{70–76} However, because of the low solubility of Mg in carbonate-enriched alkaline media, the mechanisms taking place in cementitious systems might differ, and this requires further analysis.

Questions have also been raised about the thermodynamic stability of MgCO₃·3H₂O, which is identified as the main hydrous magnesium carbonate binding phase in many reactive MgO cements. MgCO₃·3H₂O itself has been widely studied as a mineral phase for carbon sequestration [along with MgCO₃ and Mg₅(CO₃)₄(OH)₂·4H₂O] within geological formations and Mg-bearing wastes^{77–82} because of the ready formation of MgCO₃·3H₂O by interaction of magnesium-bearing minerals

and CO_2 . Claims have been made that $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is a stable product up to $\sim 100^\circ\text{C}$,^{83,84} but others have asserted that $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is instead metastable.⁸⁵ Recent research on $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ highlights the differing effects of the analytical conditions under which $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is studied on its reported thermal stability. There is compelling evidence that dehydration can occur at temperatures of $<100^\circ\text{C}$,⁸⁶ with mass loss beginning at 55°C ⁸⁷ under an atmosphere of flowing nitrogen, whereas decomposition in water can occur at $\sim 50^\circ\text{C}$.⁸⁸ Several studies have also noted the transformation of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ to $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ at $\sim 52^\circ\text{C}$.^{89,90}

Earlier experimental research by Robie and Hemingway indicated that $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is unstable at room temperature, decomposing to release CO_2 and H_2O over time when it is held under ambient CO_2 conditions.⁹¹ In that study, the authors sealed a 43-g sample in a flask with a rubber stopper, which, upon opening 4 months later, was reported to be "...accompanied by a violent expulsion of gas and some sample, much like that of a bottle of warm champagne which had been shaken before opening".⁹¹ In 1999, Königsberger et al. undertook thermodynamic modeling of the $\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$ system, concluding that, under conditions of $P_{\text{CO}_2} \leq 1$ atm, nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) is never more stable than hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$].⁹² Recent thermodynamic calculations by Chaka and Felmy are in agreement with these observations, indicating that hydromagnesite is more stable at room temperature.⁹³ This issue was recently discussed in the context of reactive MgO cements,⁹⁴ with the conclusion that caution is required in the application of such cementing systems, as the changes in crystal composition, volume, and morphology that would take place during the conversion of nesquehonite into hydromagnesite can be expected to fundamentally weaken the structure of these binders during their service life and also to lead to dimensional instability of the materials as a whole (Figure 3).

2.4. Carbonated Magnesia (MgO) Blocks

The formation of PC-free carbonated MgO binders was demonstrated by Dheilly et al.,⁹⁵ who studied the influence of $\text{Mg}(\text{OH})_2$ in lime mortars. Their study involved three mortar formulations, namely, $\text{Ca}(\text{OH})_2$ only, 50:50 $\text{Ca}(\text{OH})_2/\text{Mg}(\text{OH})_2$ blend, and $\text{Mg}(\text{OH})_2$ only, which were cured for 120 days either in air or in a CO_2 atmosphere (98% RH). Higher compressive strengths were obtained in the $\text{Mg}(\text{OH})_2$ -only mortars (8.1 MPa) after carbonation than in the $\text{Ca}(\text{OH})_2$ -only mortars (5.3 MPa). This was credited to the precipitation of hydromagnesite in the higher strength mortars through carbonation of $\text{Mg}(\text{OH})_2$, forming an interlocking network that improved cohesion. De Silva et al.⁹⁶ also studied compacted $\text{Mg}(\text{OH})_2/\text{Ca}(\text{OH})_2$ blocks, carbonated using CO_2 at 2 MPa (approximately 20 atm) pressure. It was found that, when using mostly $\text{Mg}(\text{OH})_2$, stronger blocks were formed than when using $\text{Ca}(\text{OH})_2$ (as shown in Figure 4), with $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ identified as the major carbonated Mg phase at this very elevated partial pressure of CO_2 . This stands in contrast with the results of Dheilly et al.,⁹⁵ who identified hydromagnesite as the major carbonate phase when treatment was carried out at atmospheric pressure. The long-term stability of these blocks has not been studied beyond the observation from the data in Figure 4 that the carbonated systems based on $\text{Mg}(\text{OH})_2$ alone and on 10:1 $\text{Mg}(\text{OH})_2/\text{Ca}(\text{OH})_2$ decreased in strength from 1 to 28 days of age. The findings discussed in the preceding section regarding the thermodynamic stability of

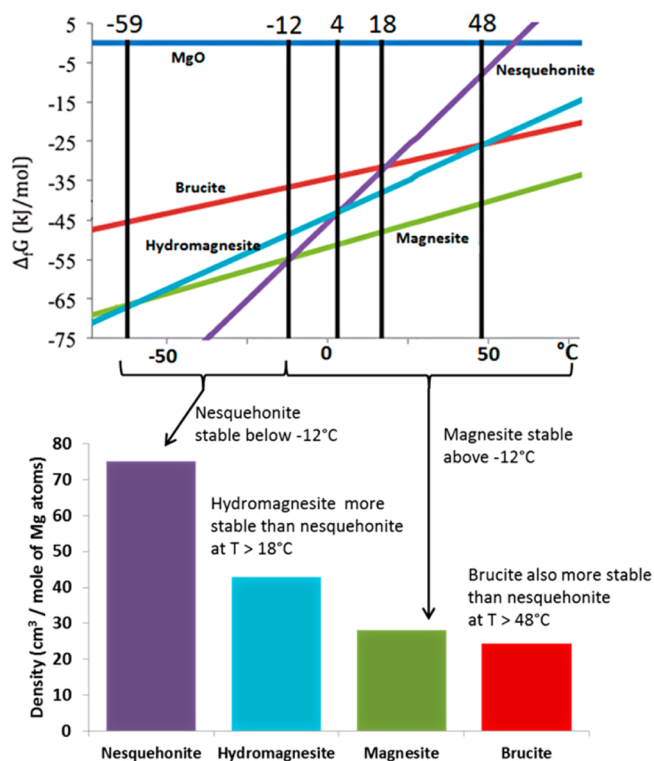


Figure 3. Free energy phase diagram for hydrous magnesium carbonates per mole of Mg ,⁹⁴ adapted from ref 93, under conditions of $P_{\text{CO}_2} = 400$ ppm and $P_{\text{H}_2\text{O}} = 32$ mbar (saturation vapor pressure at 298 K), along with the densities per mole of Mg atoms of stable magnesium phases.

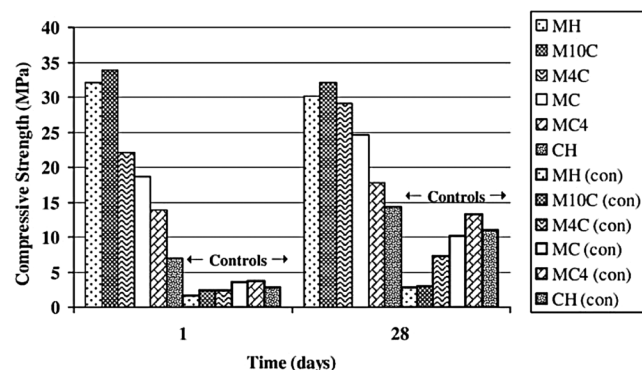


Figure 4. Compressive strengths at 1 and 28 days of $\text{Mg}(\text{OH})_2$ - $\text{Ca}(\text{OH})_2$ compacts, with molar ratios as denoted in the legend, exposed to CO_2 for 0.5 h at 2 MPa (denoted con for control) and then for 24 h at 24°C and 50% RH. The 10:1 $\text{Mg}(\text{OH})_2/\text{Ca}(\text{OH})_2$ compact (M10C) attains the highest strengths under this carbonation regime.⁹⁶ Reprinted with permission from ref 96. Copyright 2009 Elsevier Ltd.

hydromagnesite over nesquehonite under ambient conditions might be important in understanding such behavior.

Research on the use of reactive MgO cements to produce masonry blocks continued through the work of Liska and Al-Tabbaa²⁷ and Liska et al.,⁹⁷ who studied MgO/FA blends that were mixed with sand and gravel to make blocks of sufficient porosity to enable their complete carbonation. Investigations began using MgO blended with FA or Lytag (a synthetic aggregate formed from sintered coal ash) that was pressed into blocks and exposed to both natural and accelerated (20% CO_2 ,

98% RH, ambient pressure) carbonation conditions.⁹⁷ In samples cured for up to 196 days under natural conditions, no magnesium carbonates were formed; instead, consistent with the work of Vandeperre et al.,⁶³ $\text{Mg}(\text{OH})_2$ was the primary phase formed. Under accelerated-carbonation conditions, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$ were identified, with compressive strengths of up to 20 MPa achieved in some samples.⁹⁷ Further refinement of processing conditions led to the production of MgO-based blocks reaching strengths of 22 MPa after only 14 days,²⁷ which are similar to the strengths of many commercially available masonry units and thus offer a pathway for the uptake of this technology as a replacement for bricks or PC-based masonry blocks. The detailed identification of the phase equilibria, particularly the nature and stability of the magnesium carbonates present as a function of sample curing and conditioning, is still under discussion in some of these systems,⁹⁴ with $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ and dypingite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$] sometimes difficult to identify conclusively from the available data.

These works do, however, confirm that conditions with both elevated CO_2 and elevated relative humidity are required for the production of a useful product, with limited strengths observed under atmospheric curing conditions. This would limit the technology to precasting applications, where curing can be controlled in a factory, rather than application on-site.

2.5. Novacem

Another group who attracted significant attention to their work on magnesium carbonate binders was the company Novacem, which was born out of research conducted at Imperial College London, based on carbon-negative cement technology.⁹⁸ The Novacem company was liquidated in 2012, but its technology and intellectual property were sold to Calix, an Australian carbon-capture and minerals processing company.

The publicly accessible information regarding the technology behind Novacem was presented in a series of patent applications. The patent granted under the title “Binder composition”²⁹ described a porous MgO cement that takes up CO_2 during hardening and that contains no PC. The particular improvements Novacem claimed over other MgO blocks were the ability to use either MgO or $\text{Mg}(\text{OH})_2$ (or a blend thereof) as starting materials, along with the addition of a magnesium hydroxycarbonate (which can itself be produced through partial recarbonation of MgO⁹⁹) and a hygroscopic salt. The patent claimed that the hydration of MgO in the presence of these carbonates produces $\text{Mg}(\text{OH})_2$ crystals with larger surface area and, thus, a higher early strength. The addition of magnesium hydroxycarbonates was also believed to increase the rate of MgO hydration and provide nucleation sites for carbonation.¹⁰⁰ The material carbonates over time, under atmospheric conditions, assisted by the high humidity induced by the presence of the hygroscopic salt. The high-surface-area $\text{Mg}(\text{OH})_2$ in this application was claimed to be more susceptible to carbonation, a desirable characteristic when compared to previously developed MgO-based blocks. It was claimed that a net absorption of 0.59 tonnes of CO_2 per tonne of MgO can be achieved by this processing pathway, hence the advertising of the material as a carbon-negative cement.²⁹ The examples provided showed a maximum compressive strength of 25 MPa, and the example applications were limited to use as mortars, masonry block replacements, roof tiles, and bricks, which do not require high strengths and are sufficiently porous to allow carbonation.

The addition of hygroscopic salts was a key step in the success of this process, as the formation of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ from $\text{Mg}(\text{OH})_2$ (eq 8) requires both CO_2 and H_2O , meaning humidity is an important factor.

Unfortunately, the chloride salts that are described as offering attractive hygroscopic properties can induce corrosion in steel and can also become mobile under capillary action leading to efflorescence, meaning that care is required in specifying these materials for use under appropriate service conditions.

Novacem also applied for a patent that outlined the production of MgO from magnesium silicates, such as olivine ($\text{Mg,Fe})_2\text{SiO}_4$,¹⁰¹ through supercritical carbonation (temperatures of 100–225 °C, under a > 75% CO_2 atmosphere at pressures of 7.1–9.7 MPa) to form a magnesium carbonate or hydroxycarbonate and silica or metal silicates. For forsterite, which is the magnesium end member of the olivine family, this process is summarized as



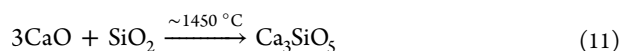
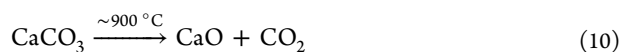
The magnesium carbonate can be calcined to produce MgO, the silica can be either utilized or discarded, and the CO_2 can be recycled. The energy requirements and consequent commercial viability of this process have yet to be demonstrated on an appropriate scale. However, the carbonation of magnesium silicates, especially serpentine minerals (such as chrysotile, lizardite, and antigorite), for CO_2 capture in geological formations is a fast-moving area of research, which could drive down costs through innovation.^{81,102,103} If this process is viable and implemented using clean sources of energy, it has the potential to produce a low-carbon cement that could be applicable for preformed blocks and tiles. Recent articles by Gartner and Macphee¹⁰⁴ and Gartner and Hirao¹⁰⁵ provide detailed reviews of the early work of Novacem and offer further insight into MgO cement carbonation in context with work on other novel binders, in both thermodynamic and practical senses.

2.6. Limitations of Carbon Sequestration

Other than under extreme carbonation conditions, reactive MgO added to PC has not been observed to carbonate at a sufficient rate to enable utilization of the higher strength (generally by a factor of approximately 4–5) of carbonated compared to uncarbonated MgO-based blocks in a practical sense. Porous MgO blocks without PC addition have, however, been shown to carbonate under mildly elevated CO_2 partial pressures. Ensuring the green credentials of these blocks would require the commercial production of the blocks to take place alongside a large point-source CO_2 emitter (e.g., a PC plant or fossil-fuel-fired power station), and considerable storage capacity would be needed for extended-duration CO_2 curing. To date, research has focused on porous blocks for masonry applications, which tend to be commodity products of low economic value, meaning that the economically viable construction of a facility to produce low-margin products would seem to depend on external drivers such as carbon taxation rather than being profitable on a simple product-for-product basis.

A common argument in favor of MgO cements is based on the perceived green credentials of MgO compared to PC because of the amount of CO_2 released during production of the latter. Most commercially available MgO is produced through the calcination of magnesite (eq 1). To produce reactive MgO, magnesite is typically calcined at <750 °C⁵⁶ (see

section 1.2), which is lower than the processing temperature used in PC production, which must usually be around 1450 °C to convert limestone and silica to the tricalcium silicate (Ca_3SiO_5) that comprises ~60% of a modern PC, in a rotary kiln,^{44,106} as follows



The use of magnesite is therefore a potential source of CO_2 savings through reduced energy requirements.

On a molar basis, magnesite and calcite release the same amounts of CO_2 during calcination. However, on a mass basis, magnesite calcination produces more CO_2 than calcite calcination (522 kg of CO_2 /t of MgCO_3 vs 439.7 kg of CO_2 /t of CaCO_3), simply because of the higher atomic mass of calcium compared to magnesium. Therefore, magnesite is not an inherently “green” material, so unless MgO is obtained from the calcination of naturally occurring brucite deposits, which are uncommon, or from magnesium silicates, then CO_2 is produced during manufacture. Production of MgO for these cements from seawater or brine has also been proposed, but as earlier noted, this process is very energy-intensive and utilizes limestone or dolomite, which releases CO_2 during processing into lime or dolime.

Furthermore, confusion in the academic and commercial literature related to MgO production has led to some inflated assumptions regarding CO_2 savings. For example, the Novacem (now Calix) patent²⁹ claims that the “high CO_2 absorption ability of MgO (up to 1.09 tonne of CO_2 /tonne MgO) offers the unique potential to develop ‘carbon negative’ concrete and concrete products”—however, this assumes little or no CO_2 emissions during the manufacture of MgO . At best, reactive MgO cements derived from carbonate precursors will be able to absorb as much CO_2 as is released during the calcination of MgCO_3 , assuming that renewable energy is used during calcination, that no other emissions occur during the supply chain, and that 100% of the MgO is carbonated during curing or in service.

2.7. Conclusions

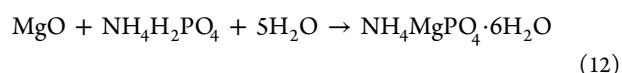
Reactive magnesia cements have not yet been demonstrated to perform successfully under ambient conditions, as they require production as porous units or structures, control of internal humidity, and enhanced levels of CO_2 to form binding magnesium carbonate phases. Once produced, these cements have been shown to form strong enough products for use as precast materials, especially blocks or tiles, although the long-term durability of the formed phases is currently in question. It is imperative for the success of these cements that MgO can be produced economically and sustainably from either magnesium silicate or brines at a commercially sustainable throughput. Ultimately, reactive magnesia cements are not simply classified as “eco cements”, as has been done in some areas of the literature, although there is certainly scope for this classification to be achieved. Examples that have been confirmed to form carbonates are (for the moment) confined to porous products exposed to elevated CO_2 curing conditions. These materials do have some potential for becoming carbon-neutral, if produced from naturally occurring brucite deposits, using renewable fuels for calcination and ensuring carbonation throughout the product. Carbon-negative cements could potentially be produced from magnesium silicate sources, offering interesting

scope for the replacement of PC in the production of unreinforced blocks and other precast or factory-produced units, but with limitations in large-scale in situ concreting or where mechanical loading necessitates the use of steel reinforcement.

3. MAGNESIUM PHOSPHATE CEMENTS

3.1. Phosphate Bonding of MgO

Magnesium phosphate cements are formed through an acid–base reaction between MgO and a soluble acid phosphate (typically an ammonium or potassium phosphate), forming a magnesium phosphate salt with cementitious properties as exemplified by the equation

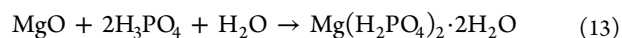


This class of materials is known broadly as magnesium phosphate cements (MPCs).

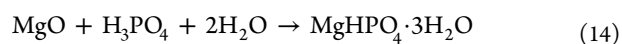
The application of phosphate bonding to produce cementitious materials has long been known, with some of the earliest such records from the late 19th century describing zinc phosphate dental cements.^{107,108} Phosphate-bonded refractories are also in widespread use, exploiting the property of cold setting to form products that are stable at high temperatures. One of the first systematic studies of the phosphate bonding process was published by Kingery in 1950,^{109–111} who remarked that acid phosphates are responsible for bonding in cold-setting systems and stated that “For optimum bonding, a weakly basic or amphoteric cation having a moderately small ionic radius is required”. Describing the then-existing literature on oxide reactions with phosphoric acid, Kingery noted that acid or inert oxides do not react with phosphoric acid, whereas highly basic oxides react violently, forming porous structures with decreased strengths. Weakly basic or amphoteric oxides perform the best, with oxides of Be^{2+} , Al^{3+} , Fe^{3+} , and Mg^{2+} giving the best results in order of bond strength.^{110,111}

Considerable literature exists for zinc phosphate cements, because of their use as dental cements.^{112–114} However, these cements set much too rapidly for use as cements for construction purposes, whereas the ability to produce dead-burned MgO , with reduced reactivity (see section 1.2), has opened the possibility for the production of MPCs suitable for structural applications. Such MPCs have been the subject of several patents for use as refractory investments, commonly to cast alloys, and often for use in dentistry. For example, in 1940, Prosen outlined a dental investment using silica, MgO , and a blend of ammonium and sodium phosphates.¹¹⁵

Formation of magnesium phosphates through this acid–base process can be simply achieved through the reaction of MgO with H_3PO_4 .^{110,116} Finch and Sharp¹¹⁶ found that when starting from a 1:1 molar $\text{MgO}:\text{H}_3\text{PO}_4$ aqueous mixture, a hard though water-soluble product was formed and the reaction stoichiometry deviated from the theoretical 1:1 case through incomplete reaction of the MgO , resulting in a 1:2 product as exemplified in eq 13.



To form an insoluble product with a 1:1 ratio of Mg to P , an excess of MgO is typically required,¹¹⁷ with the reaction instead proceeding through eq 14.



These reactions are highly, often violently, exothermic, which raises practical challenges regarding the use of this process on a large scale.

3.2. Application as Cements

Applying the magnesium-phosphate bonding process to the production of cementitious products requires a system that reacts more slowly and with a more gradual heat evolution. In the 1940s, Every and Prosen each filed patents using MgO and ammonium phosphates to form molded products,^{115,118} which reacted more slowly than systems using phosphoric acid, and these ammonium-containing compositions formed the focus of much development in the ensuing decades. The combination of MgO with phosphoric acid and $\text{Al}(\text{H}_2\text{PO}_4)_3$ has also been used in some refractories, forming a moldable product consisting of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and an amorphous aluminum phosphate phase.^{116,119}

A key step toward the formulation of modern MPCs was provided by Limes and Ponzani of the Republic Steel Corporation. Their 1966 patent¹²⁰ outlines a refractory cement that can be sprayed onto furnace walls and is tolerant of both high and low temperatures. As MgO mixed with phosphoric acid reacts too rapidly for spray application, they proposed the use of a blend of liquid ammonium ortho-, pyro-, and polyphosphates with dead-burned MgO and succeeded in producing a cold-setting sprayable composition.¹²⁰

The ability to use these quick-setting cements for other purposes was realized when rapid-repair cements began to be marketed under various trade names by the early 1970s¹²¹ and were generally shipped as a dry powder mix, to which a liquid phosphate solution was added. A number of patents pertaining to these cements were published in 1974–1977 describing the use of magnesium ammonium phosphates as rapid patch repair cements for roads and highways.^{122–125} Among these, Stierli et al. of W.R. Grace & Co. proposed the addition of a boron compound such as borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) to control the rate of reaction, which was claimed to delay setting for up to 1 h to offer a more convenient working time.¹²⁵

Several reports in the 1980s show that interest remained in MPCs for repair of damaged runways, pavements, and bridges.^{126,127} Notably, a report detailing the use of MPC to repair a runway after the Falklands War described compositions setting in ~30 min, enabling patching of over 1000 “scabs” to enable rapid recommissioning of Port Stanley Airport.¹²⁸

However, continued development of lower-cost options, such as blended PC compositions, rapid-setting high-alumina cements and epoxy resins, has left MPC as a marginal player among currently marketed rapid-setting mortars. A more recent evaluation of proprietary rapid-repair mortars showed many non-MgO mortars equaling or exceeding the properties of leading MPCs.¹²⁹ The release of gaseous ammonia from the hardening and hardened cements also places some restrictions on the use of these materials on environmental and hygiene grounds.

3.3. Method of Action

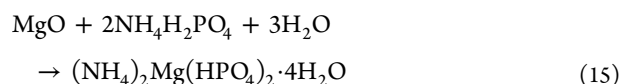
The scientific literature on the chemical specifics of MPCs did not emerge until the early 1980s. Among the early publications were two articles by Sugama and Kukacka in 1983,^{130,131} which described the testing of cements made from MgO and diammonium phosphate solutions and from MgO and ammonium polyphosphate solutions. The principal products formed were claimed to be struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) and

$\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, along with small quantities of newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) and $\text{Mg}(\text{OH})_2$.^{130,131}

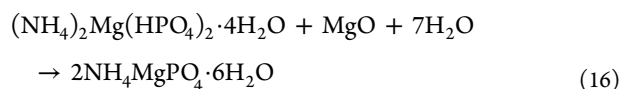
Abdelrazig and Sharp¹³² disagreed with these findings, claiming that mixtures of MgO and monoammonium phosphate form dittmarite ($\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$) and that the addition of sodium tripolyphosphate as a setting retarder resulted in the formation of struvite and schertelite [$\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$].¹³² This was clarified by Popovics et al. in 1987,¹³³ who identified that dittmarite forms as the principal product if setting is rapid (i.e., without a setting retarder), whereas struvite is the principal product if setting is slow.

Although earlier patents and articles used liquid polyphosphates or diammonium phosphate, by the late 1980s, MgO and powdered monoammonium phosphate were the preferred materials, shipped as dry powders, principally forming a crystalline struvite binding phase when mixed with water, according to eq 12.¹³⁴

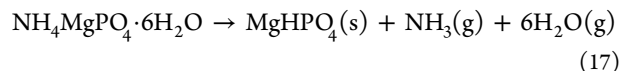
Further investigations by Abdelrazig et al.¹³⁴ of an MPC retarded with sodium tripolyphosphate showed struvite to be the main phase, although with some schertelite and minor traces of dittmarite and stercorite. It was suggested that schertelite is an intermediate phase in the formation of struvite, first forming through the reaction



and then reacting with more MgO and H_2O through



The formation of minor quantities of dittmarite in MPCs is thus related to the presence of insufficient water during hydration or the in situ dehydration of struvite due to autogenous heating of the cement because of its highly exothermic hydration reaction process,^{135,136} which can induce an increase in temperature to at least 80 °C.¹³⁵ Struvite was demonstrated to be unstable from 50 °C in air, decomposing through the reaction¹³⁶

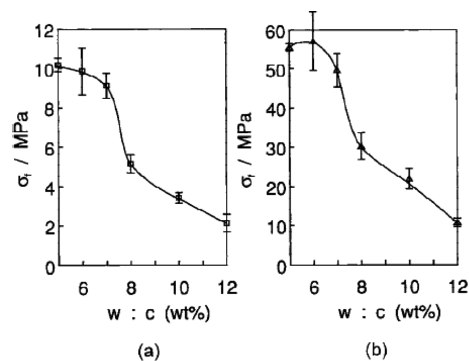


The MgHPO_4 thus formed, which is often X-ray amorphous, can rehydrate to form newberyite. However, boiling of struvite in water leads only to the loss of water, forming dittmarite, which can then rehydrate to reform struvite at room temperature.¹³⁶ Depending on the heat evolved by hydrating MPC and the availability of water, such a process could account for the dittmarite identified in some rapid-setting MPC formulations.¹³³ The mineral phases identified within various MPCs are listed in Table 3.

The principal sources of variation in performance and properties among modern MPC systems relate to the quantity of water used, the magnesium/phosphate ratio, the addition of diluents, and the use of setting retarders. The effect of water content on the cements is notable. As is typical for cements, increasing the water content of a mixture is reported to decrease the compressive and flexural strengths,^{133,135,137} as demonstrated in the results of Hall et al.¹³⁵ shown in Figure 5. The addition of water beyond 20 wt % has been reported to cause MPCs to “split”, meaning that the cement remains as a

Table 3. Magnesium Phosphate Minerals Reported in MPCs

mineral	formula
struvite	$\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$
newberyite	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$
hannayite	$(\text{NH}_4)_2\text{Mg}_3\text{H}_4(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$
schertelite	$(\text{NH}_4)_2\text{MgH}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$
dittmarite	$\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$
stercorite	$\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$
struvite-K	$\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$

**Figure 5.** Effects of water content (expressed as water/cement mass ratio, in percentage) at 7 days on the (a) flexural and (b) compressive strengths of MPC mortars. Reproduced with permission from ref 135. Copyright 2005 John Wiley & Sons.

slurry and does not functionally set,¹³⁸ distinct from the case for PC, where the addition of an excess of water means that the paste segregates and “bleeds” excess water, forming a solid (although porous) hydrate product and a clear supernatant solution.

To form the maximum possible amount of struvite as a binding phase, a stoichiometric 1:1 molar ratio of MgO to $\text{NH}_4\text{H}_2\text{PO}_4$ would theoretically be preferred. In typical usage, however, MgO is used in significant excess, as excess unreacted phosphate would be soluble, leaching out of the cement during service, potentially compromising structural integrity but also leading to unappealing efflorescence on the cement surface. Although numerous studies on this topic have been undertaken, comparison of published research on struvite-based cement systems is hampered by wide variations in the use of retarders and the proportions of water used, along with a disinclination to report whether molar or weight ratios are used.^{139,140}

For struvite-K systems (cf. section 3.4), a few more detailed studies have been undertaken, with Mg/P molar ratios of 4–6 producing the highest compressive strengths and higher ratios yielding a reduction in strength.^{141–143} These works did not, however, study low or equimolar ratios of Mg/P, which remains a notable gap in the understanding of these cements.

The use of high Mg/P ratios results in the presence of large quantities of unreacted MgO in these cements once set. In general construction practice, the presence of free MgO in hardened cements is considered highly undesirable and a harbinger of future expansive cracking as it slowly hydrates to $\text{Mg}(\text{OH})_2$.¹⁴⁴ Long-term studies of MPC durability and dimensional stability are not prominent in the open literature; however, the presence of MgO might not be a major issue in these cements, as it has been reported that struvite forms around MgO grains, effectively entombing them.^{132,145} An excess of MgO is thus required to react with all of the phosphate, as a significant fraction of the MgO remains

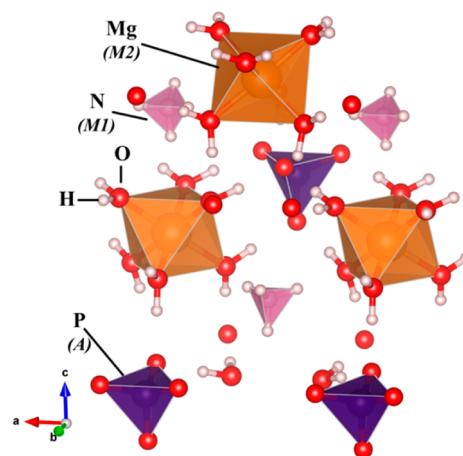
inaccessible for reaction, with the optimal ratio depending on the particle size and reactivity of the MgO.

3.4. Struvite-K Cements

Crystalline magnesium ammonium phosphates are well-known mineral phases occurring in nature, principally in bat guano. The main crystalline phase in modern MPCs is struvite. This phase was first described by Teschemacher in 1845, occurring as crystals in guano at Saldanha Bay, now in South Africa, and named as the mineral guanite.¹⁴⁶ Also in 1845, Ulex^{147–149} reported the discovery of this mineral in Hamburg during the reconstruction of St. Nicholas church on the site of the former Neue Burg, which had been destroyed in 1072. Crystals up to 2.5 cm in length were unearthed in a buried ditch, presumed to have been used to store waste and manure and as an open dung pit. Ulex postulated that the crystals formed because of “infiltrations of urine through a soil consisting of vegetable matter” and named the new mineral after Heinrich von Struve, a well-known diplomat and mineralogist at the time.^{147–149}

Struvite was later reported in 1870 in bat guano from the Skipton caves in Victoria, Australia.¹⁵⁰ Several other magnesium phosphates were also discovered in this guano over the next few decades, including hannayite, newberyite, schertelite, and dittmarite.^{151–153} As listed in Table 3, these are all also important phases in synthetic MPCs.

The struvite mineral family is known to accept a wide range of substituents within the $\text{M1M2A} \cdot 6\text{H}_2\text{O}$ structure (Figure 6).

**Figure 6.** Crystal structure of struvite, drawn from ref 154, with M1, M2, and A sites identified in italics.

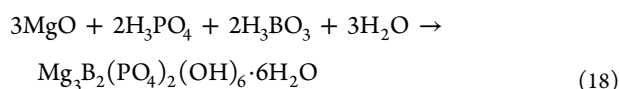
These include substitutions of monovalent cations at the M1 site (NH_4^+ , K^+ , Rb^+ , Cs^+ , Tl^+), divalent cations at the M2 site (Mg^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Cd^{2+} , Cr^{3+} , Mn^{2+} , VO_2^+), and trivalent oxyanions at the A site (PO_4^{3-} , AsO_4^{3-}).^{155–163}

A considerable quantity of struvite research pertains to its role in urinary stones¹⁶⁴ and as a precipitate that causes blockages in wastewater works.^{165,166} The tendency of struvite to precipitate from municipal wastewater has led to commercial recovery of phosphate and nitrogen from waterworks as struvite for sale as a fertilizer, but this can lead to problems related to the coprecipitation of heavy metals within the struvite structure.^{167–171} Although potentially problematic for the phosphate recovery industry, this ability is of interest for the immobilization of heavy metals and radionuclides within MPCs, particularly those based on an ammonia-free magnesium potassium phosphate binding phase such as struvite-K. This

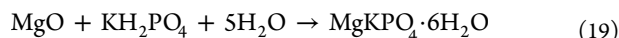
phase ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$) has been found as a naturally occurring alteration mineral,^{172,173} but it has been popularized over the past 20 years as an alternative MPC cement binder.

Ammonia-free MPCs were popularized by Wagh, Singh and other workers from Argonne National Laboratory as an encapsulant for various nuclear wastes arising from the cleanup of legacy nuclear sites in the United States. This began in the early 1990s with research on the use of MPCs that can tolerate ash- and salt-bearing wastes, combined with radioactive and heavy-metal contaminants. Typically, these wastes might include pyrophoric materials, requiring a low-temperature encapsulation process, as well as salts or materials that are unsuitable for cementation in conventional PC blends.^{174–179}

Initial development focused on the use of a zirconium phosphate matrix to chemically immobilize wastes, with encapsulation of this phase in a magnesium phosphate binder formed from MgO , boric acid (H_3BO_3) as a setting retarder, and phosphoric acid.^{180,181} In a quick-setting (15 min) reaction, newberyite and lüneburgite [$\text{Mg}_3\text{B}_2(\text{PO}_4)_2(\text{OH})_6 \cdot 6\text{H}_2\text{O}$] were reportedly formed^{180,181} through eq 14 and the reaction



Although this newberyite-based wasteform reportedly performed well during leach testing, the use of phosphoric acid generated too much heat during setting (large-scale systems showed boiling of the mixture), and its acidity was problematic in a processing sense.¹⁷⁶ This issue was overcome through the use of KH_2PO_4 instead of phosphoric acid,¹⁷⁶ creating struvite-K through the reaction



The reduced acidity of KH_2PO_4 yields a slower and more controlled reaction and therefore resolves issues with heating.¹⁸² Being a dry powder, KH_2PO_4 can also be prebagged with MgO similarly to $\text{NH}_4\text{H}_2\text{PO}_4$ in modern ammonium-MPC repair mortars, but avoiding the evolution of ammonia gas during setting. It is also one of the least soluble of the commercially available acid phosphates (see Table 4), which is advantageous compared to the sodium analogue.

Table 4. Solubilities of Selected Acid Phosphates in Water¹⁸³

phosphate	solubility at 25 °C, 1 bar (g/100 g of H_2O)
KH_2PO_4	25.0
$\text{NH}_4\text{H}_2\text{PO}_4$	40.4
NaH_2PO_4	94.9

These magnesium potassium phosphate cements (MKPCs) are also described as “chemically bonded phosphate ceramics (CBPCs)”¹⁸⁴ or by the trade name “Ceramicrete” and have been extensively developed and trialed in the United States and Russia for conditioning of various challenging nuclear wastes,¹⁸⁵ including plutonium-contaminated ash;¹⁷⁴ heavy-metal and radium wastes;¹⁷⁸ ^{99}Tc -bearing wastes, using SnCl_2 as a reductant;¹⁷⁷ liquid Hanford vitrification wastes;¹⁸⁶ and Mayak salt wastes.¹⁸⁷

Alongside this application, other MKPC patents have been granted to Wagh, Singh, and co-workers,^{188–190} including for sprayable compositions and oil-field applications.

MKPCs have also been proposed as lower-pH binders for reactive metal wastes, such as aluminum wastes arising from

nuclear operations. Aluminum corrodes in alkaline media, such as conventional PC blends,¹⁹¹ reacting expansively and cracking the cement while producing flammable hydrogen gas. This means that the lower internal pH of struvite-K-based cements can be advantageous in reducing corrosion of aluminum.^{184,192,193} For this application, MKPCs were tested for in situ cementation of the P-reactor vessel at the Savannah River Site in South Carolina during decommissioning, but ultimately, a sulfoaluminate cement was preferred for large-scale use.^{194,195} In the United Kingdom, MKPCs have been investigated for the encapsulation of reactive metallic aluminum-, magnesium-, and uranium-containing nuclear wastes.¹⁹⁶ The low water content at which MKPCs can be formulated¹⁹⁶ also reduces the availability of free water for corrosion of Mg and U.¹⁹³

Interest in MKPCs has, however, extended beyond the nuclear industry, and most current literature focuses on MKPCs rather than ammonia MPCs.

3.5. Retardation of MPCs

The ability to control the rate of reaction in MPCs is crucial to the application of these cements, whether in rapid patch repair or low-temperature waste encapsulation. With NH_4 -MPCs, the need to produce a premixed “just-add-water” bag of cement led to the development of retarders. Addition of water to a blend of monoammonium phosphate and MgO results in a mass that sets too rapidly to be of use, and thus, early MAP patch repair cements used a separately packaged ammonium polyphosphate solution that reacted more slowly with the MgO . Several alternative methods have been used over the years, although the addition of borates has now come to be favored.

3.5.1. Temperature. Although MPCs are capable of setting at temperatures below freezing, the acid–base reaction is considerably slowed. This has been encountered in practice during patch repair in Alaska¹⁹⁷ and was studied by Yang and Wu,¹³⁹ who demonstrated an MPC mortar capable of setting at -10 °C in a period only 3 times longer than that at 25 °C , as illustrated in Figure 7. Such low temperatures pose a challenge

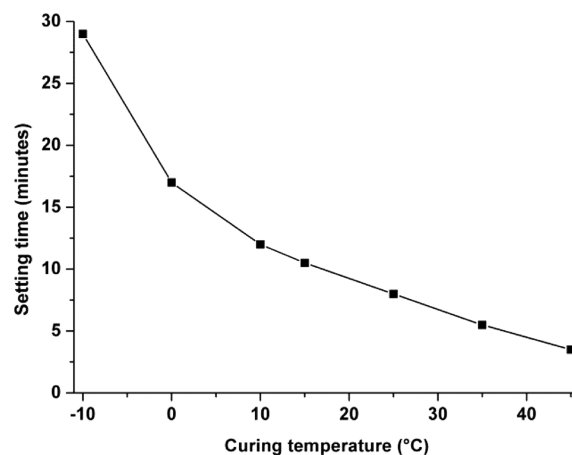


Figure 7. Effect of temperature on ammonia-MPC setting time (with 5% $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), drawn from data presented in ref 139.

to most other cementing systems, as the setting of many cements is problematic below 0 °C , but the inherently rapid reaction and low water content of MPCs are advantageous in this context.

3.5.2. Sodium Tripolyphosphate. Sodium tripolyphosphate ($\text{Na}_3\text{P}_3\text{O}_{10}$) was an early retarder used in NH_4 -MPCs and

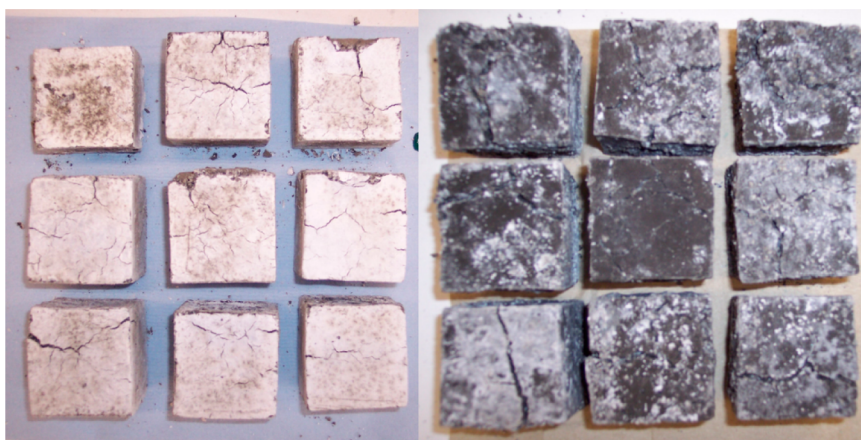


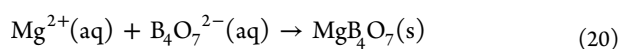
Figure 8. Photographs of 50-mm cubes of MKPC blast-furnace slag (BFS; left) and MKPC fly ash (FA; right), each with a 1:1 ratio of MKPC to diluent, suffering from expansion and cracking 3 days after casting.²⁰⁸

was generally added into the mixes as a powder, to increase MPC setting times from 4–7 to 15 min.^{134,198} $\text{Na}_5\text{P}_3\text{O}_{10}$ has been proposed to chelate Mg^{2+} ions from the MPC slurry,¹³⁴ but its effectiveness is restricted by the limited solubility of $\text{Na}_5\text{P}_3\text{O}_{10}$ in an already saturated acidic phosphate solution during MPC setting reactions.¹⁹⁸ The addition of $\text{Na}_5\text{P}_3\text{O}_{10}$ also has the side effect of promoting the formation of stercorite ($\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$) in ammonium phosphate cements,¹⁹⁹ although the effects of this phase on MPC properties and performance are unknown.

3.5.3. Borates. More recently, borate has become the de facto standard retarder for MPCs because of its effectiveness and the relatively low doses required compared to $\text{Na}_5\text{P}_3\text{O}_{10}$. Both $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and H_3BO_3 have been widely used, with similar effects, although H_3BO_3 has been more widely used in recent years. With the inclusion of both $\text{Na}_2\text{B}_4\text{O}_7$ and H_3BO_3 in the EU Candidate List of Substances of Very High Concern for Authorisation²⁰⁰ because of reproductive toxicity, the use of these substances in Europe is becoming restricted, but this is not yet the case globally.

This retarding mechanism was originally developed to extend the pot life of NH_4 -MPC in high temperatures (e.g., road patching in the summer sun), with Stierli et al.'s patent¹²⁵ reporting the use of ammonium pentaborate [$(\text{NH}_4)_5\text{B}_5\text{O}_{18} \cdot 8\text{H}_2\text{O}$], $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, H_3BO_3 , and trimethyl borate [$\text{B}(\text{OCH}_3)_3$] as retarders. With boron compounds added at a concentration of several weight percent, setting times of up to 30 min could be achieved, allowing for the marketing of a preblended one-bag cement. The addition of larger quantities of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (20 wt %) reduced compressive strength development during early aging, although the reduction was only 8% after 28 days of curing.²⁰¹

The precise retarding mechanism of boron compounds in MPCs is currently unclear. Yang and Wu¹³⁹ concluded that the Mg/B ratio affects setting but the B/P ratio does not, indicating that the borates are reacting with the MgO. Sugama and Kukacka¹³¹ initially suggested that retardation was due to the Mg^{2+} ions being chelated by $\text{B}_4\text{O}_7^{2-}$ ions, forming a colloidal precipitate around MgO grains, reducing further dissolution and thus retarding strength development.¹³¹ This would follow the known action of $\text{Na}_2\text{B}_4\text{O}_7$ as a water softener²⁰²



Conversely, Hall et al.¹⁹⁸ suggest that $\text{B}_4\text{O}_7^{2-}$ ions are unlikely to form in the acidic phosphate (pH ~ 5) solution of a freshly mixed MPC slurry and instead proposed that $\text{B}(\text{OH})_3$ or $\text{B}(\text{OH})_4^-$ adsorbs to the MgO surface, reducing its dissolution. A more recent suggestion from Wagh and co-workers is that H_3BO_3 reacts with MgO and the acidic phosphate solution to form a solubility-limiting coating of lüneburgite $\{\text{Mg}_3[\text{B}_2(\text{OH})_6](\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}\}$ ^{181,184,203} around MgO grains. This was claimed to occur in both phosphoric acid–MgO and KH_2PO_4 –MgO systems using 4 wt % or less H_3BO_3 ,^{181,184,204} but it appears likely from solubility arguments that such a mechanism would require a higher boron concentration to be truly effective.

3.5.4. Diluents. Diluents are typically unreactive filler materials added to cements to save on material costs and/or to reduce exothermic output for a massive pour. Traditional NH_4 -MPCs utilize sand as a diluent to produce a mortar, whereas MKPC mortars (often for nuclear applications) make use of finer materials such as coal fly ash,^{142,196,205} blast-furnace slag,^{206,207} and wollastonite (CaSiO_3).²⁰⁶

Among these materials, fly ash is the most popular, as its addition to an MKPC mixture also enhances fluidity through the “ball-bearing”-type effect of the spherical fly ash particles. The addition of fly ash to an MPC mortar can more than double setting times (although ≥ 50 wt % replacement of MPC is required), with a corresponding increase in fluidity.²⁰⁵ Although this reduces early (<24 h) strength, the 28-day compressive strength is increased from 72 to 75.5 MPa if 50 wt % of the MPC is replaced by fly ash.²⁰⁵ (For comparison, Portland cements and blended Portland cement are required to achieve a minimum of 32.5 to 52.5 MPa at 28 days of curing under European standards.⁶⁴) Although these diluents are often described as being nominally inert, Gardner et al.²⁰⁷ noted the potential formation of potassium aluminophosphate gels when fly ash or blast-furnace slag are combined with MKPCs, suggesting that there is, in fact, a chemical interaction taking place rather than a simple dilution process. This possibility highlights the need for this chemical reaction process to be more fully understood if these composite MKPC-based cements are to be used in critical applications such as nuclear waste immobilization.

3.6. MKPC Expansion

An under-reported yet potentially serious issue with MKPCs is that of significant deleterious expansion during setting, which

affects pastes seemingly at random. Although not noted in the scientific literature, this issue has been illustrated in several Pacific Northwest National Laboratory (PNNL) and Savannah River National Laboratory (SRNL) reports.^{186,194} During trials to scale up Ceramicrete, Josephson et al. noted severe expansion after casting small samples, popping lids off the containers used for casting the cement.¹⁸⁶ Stefanko et al. reports expansion of MKPC grouts after 24 h of curing; attempts to determine the cause of expansion were inconclusive, with only crystalline struvite-K identified.¹⁹⁴ Gardner recently reported the expansion of MKPC–slag and MKPC–fly ash blends affecting roughly one in 10 batches,²⁰⁸ of which Figure 8 shows two particularly badly affected batches.

Singh et al. attributed expansion to carbonates or bicarbonates in simulant waste streams reacting with the phosphoric and H_3BO_3 , evolving CO_2 during setting.²⁰⁶ It should be noted, however, that expansion has also been observed in the absence of any carbonates,²⁰⁸ including in pure MKPC, as well as in the materials blended with BFS or FA in Figure 8, which are unlikely to show significant thermal cracking effects because of their low heat output. This expansion has been reported only in the MKPC system, not in ammonia-MPCs, but it does represent a serious issue with MKPCs, requiring further research before these cements can be used with full confidence at an industrial scale.

3.7. Conclusions

MPCs were popularized as rapid patch repair materials using a blend of monoammonium phosphate and magnesium oxide, generally binding through an acid–base formation of struvite. This enabled rapid setting and use in cold environments that might preclude other cements. Various retarders have been implemented to extend setting times, with borates the most popular retarder today. Over the past 15–20 years, interest in MPCs has waned in favor of potassium-struvite cements, largely because of the reduced heat output and the elimination of ammonia liberation during setting. MPCs have found a niche as prospective nuclear waste immobilization matrixes, especially for the treatment of reactive metals unsuitable for conventional PC blends. However, the internal pH of MPCs is too low and the cost is too high to allow for their use in structural steel-reinforced concrete, which will continue to restrict these cements to lower-volume niche applications.

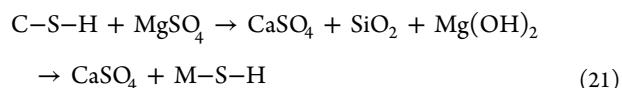
4. MAGNESIUM SILICATE HYDRATE (M–S–H) CEMENTS

The concept of using a magnesium–silicate bond to form a cementitious product has existed for over 100 years. In 1889, Cummings claimed to produce a magnesium silicate cement by mixing and calcining MgCO_3 and finely pulverized silica to form a hydraulic powder,²⁰⁹ and in 1899, Steiger proposed a cement consisting of MgCl_2 , MgO , potassium or sodium silicate, and water that formed a “hydrosilicate of magnesium and chlorid [sic] of alkali”.²¹⁰ Various other patents describe additions of soluble silicates to magnesium oxychloride cements²¹¹ and powdered asbestos-derived cements^{212–214} or simply the fusion of talc or asbestos and silica into refractory articles.^{215,216} Although proposed in many of these patents, the use of the magnesium–silicate bond as a cement-forming system remained relatively unresearched for over 50 years and is still not well understood.

The reaction of MgO with a soluble source of silica generally forms a poorly crystalline talc-like or serpentine-like phase, the

precise structure of which is still under investigation and appears to depend significantly on the Mg/Si ratio.^{217,218} Modern M–S–H cements are generally formed from a source of magnesium (typically MgO) and a source of highly reactive silica (e.g., silica fume) in situ, rather than forming from the hydration of a magnesium silicate clinker, because magnesium silicates are nonhydraulic, as noted in section 1.

Within modern cements, M–S–H first came to attention during investigations into the degradation of maritime concretes produced from PC. In 1953, Cole observed the presence of a crystalline hydrated magnesium silicate (reported as $4\text{MgO}\cdot\text{SiO}_2\cdot 8.5\text{H}_2\text{O}$) in a severely degraded seawall²¹⁹ and postulated that it had formed as magnesium salts in the seawater reacted with silica gel in the degraded cement; these results were supported by several later observations on PC-based materials damaged by MgSO_4 attack,^{220–225} according to eq 21, which schematically (and without intending to define stoichiometries of any of the reactions or silicate gels) describes the degradation of calcium silicate hydrate (C–S–H) and formation of M–S–H²²⁶



The loss of strength associated with the formation of M–S–H during MgSO_4 attack on hydrated PC led Cohen and Bentur to label M–S–H as a “noncementitious” phase.²²⁷ However, although its presence is not usually seen as beneficial to cements, M–S–H has been postulated to act as an extra binding phase for cations in cements blended with blast-furnace slag, which tends to be richer in Mg than is PC.²²⁸

4.1. M–S–H as a Cementitious Phase

The first major systematic studies of M–S–H began in the late 1980s for use as a non-PC binder in refractory castables,²²⁹ driven by Elkem as a major producer of microsilica (also known as silica fume, an amorphous silica byproduct of silicon and ferrosilicon production). This binder was based on a blend of jet-milled fine dead-burned MgO and microsilica, which can be sprayed onto a substrate, providing good resistance to temperatures up to $1500\text{ }^\circ\text{C}$.^{230,231} The high compressive strengths of these materials, up to $\sim 130\text{ MPa}$ (Figure 9), demonstrates that M–S–H is not noncementitious, as was previously claimed, but rather can form a strong bond. Szczerba

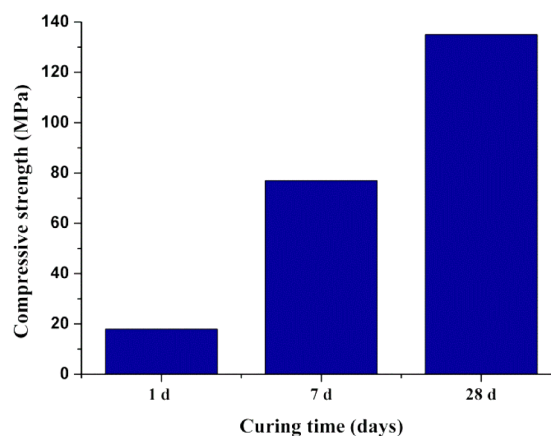


Figure 9. Compressive strength of M–S–H prisms cured underwater at $20\text{ }^\circ\text{C}$, plotted from data in ref 229.

et al.²³² also reported that M–S–H could be a useful material for refractory castables because of the high melting temperatures of MgO and forsterite (Mg_2SiO_4), two products of the thermal degradation of M–S–H.

The use of MgO and silica fume to form M–S–H was applied to cement systems in China in the mid-2000s, when patents were granted to Chen and Wei for M–S–H mortars made using MgO, silica fume, and various industrial byproducts including steel slags and coal fly ashes.^{233,234} Several mortars were claimed to reach over 70 MPa in compressive strength after 28 days of curing, verifying the ability of this binder to form a cementitious mass.

Sandberg and Mosberg²²⁹ and Wei and co-workers^{235,236} validated the use of sodium hexametaphosphate $[(\text{NaPO}_3)_6]$ to increase the fluidity of M–S–H-forming systems in the fresh state, to reduce the water/solids ratio required to achieve mixing and casting. Szczerba et al.²³² also described a factor of 10 decrease in the time required to form M–S–H when the curing temperature was increased from 20 to 40 °C. Each of these studies led to the production of a characteristically poorly crystalline M–S–H, with an X-ray diffraction pattern similar to that shown in Figure 10.

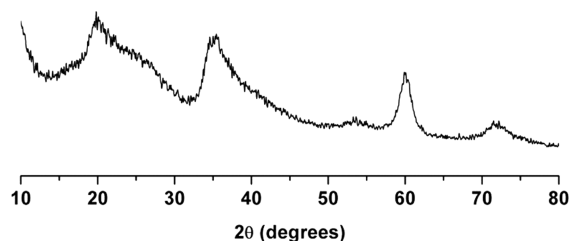


Figure 10. XRD pattern of a $\text{Mg}(\text{OH})_2$ -silica fume cement, cured at 40 °C for 8 months, showing formation of a poorly crystalline M–S–H phase.²³⁷

Recently, M–S–H cements have been studied for their potential as cements for nuclear waste immobilization, with particular focus on the less-alkaline pH characteristics of M–S–H cements compared to PC. This is considered a disadvantage in reinforced concrete applications, as the moderate pH of M–S–H does not offer effective passivation of mild steel reinforcing in the same way as the highly alkaline environment of the PC pore solution. However, this same moderate pH could enable M–S–H to be used as an encapsulation matrix for metallic aluminum wastes resulting from the nuclear industry. Zhang et al.²³⁸ studied M–S–H cements made from dead-burned MgO and silica fume, finding that the pH of these cements varied from 9.5 to 10.5, which would enable use as a lower-pH binding system, and later extended that work to the addition of MgCO_3 to reduce the initial pH, finding the corrosion of reactive aluminum to be greatly reduced.^{239–241}

The use of M–S–H cements has also been studied for the immobilization of $\text{Mg}(\text{OH})_2$ -rich Magnox sludges, a legacy waste from the U.K. nuclear industry. This motivated the use of $\text{Mg}(\text{OH})_2$ as a precursor, rather than MgO as is typically used in M–S–H cements, with the aim of using this waste as an integral part of the cementitious matrix and thus achieving a very high waste loading.²⁴²

Several countries, including France, Switzerland, Belgium, Sweden, and Finland,^{243–246} are proposing radioactive waste repositories based on a multibarrier concept utilizing clay backfills. These will require cements during construction and

plugging, the alkaline nature of which is known to locally degrade the clays, resulting in an array of alteration products and physicochemical changes over extended periods of time.^{247–252} It is instead envisaged that construction cements will be lower-pH (<11) cements to reduce dissolution of the clays and improve overall cement–clay compatibility, likely PC–silica fume (SF) or ternary PC–SF–FA/BFS^{247,253–256} blends. Although these cements have improved compatibility with the clays, studies of the interfacial zone between these low-pH cements and clays note the formation of M–S–H along with hydrotalcite.^{257,258} This research has pushed forward research into the structure of M–S–H in recent years, but also poses the question as to whether M–S–H binders themselves could be used as low-pH shotcrete and stabilizing cements in clay-based repositories. As noted earlier, research by Zhang et al.²³⁸ into M–S–H binders produced cements with pH values of 9.5–10.5, well within the range required for lower-pH cements to be considered for this use.

4.2. Structure of M–S–H

Although the understanding of M–S–H as a binding phase is in its infancy, a significant quantity of literature does exist related to the structure and nature of the M–S–H system. The minerals linked to M–S–H and selected crystal structures are noted in Table 5. Interest in the synthetic formation of

Table 5. Minerals Linked to M–S–H

mineral	group	formulation
lizardite	serpentine	$\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$
antigorite	serpentine	$\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$
chrysotile	serpentine	$\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$
sepiolite	phyllosilicate	$\text{Mg}_4(\text{Si}_6\text{O}_{15})(\text{OH})_2 \cdot 6\text{H}_2\text{O}$
saponite	phyllosilicate	$\text{Ca}_{0.25}(\text{Mg},\text{Fe})_3((\text{Si},\text{Al})_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$
talc	phyllosilicate	$\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$

chrysotile asbestos encouraged the study of the MgO – SiO_2 – H_2O system from the early 1950s, although these studies often used high pressures and temperatures using hydrothermal techniques. In 1954, Kalousek and Mui²⁵⁹ studied mixtures of MgO and silicic acid at temperatures between 75 and 350 °C, with Mg/Si ratios of 0.5–2.0. The solid reaction products were reported to be a mixture of talc (Mg/Si = 0.75) and chrysotile (Mg/Si = 1.5), exhibiting diffuse scattering in X-ray diffraction patterns. In 1960, Yang studied the MgO – SiO_2 – H_2O system from 100 to 300 °C,²⁶⁰ conducting hydrothermal synthesis of phases at pressures up to 138 MPa. A number of products were formed that were reported to resemble talc and serpentine. Both of these articles suggest that several solid M–S–H gels with differing compositions can precipitate, although whether they coprecipitate or form through an intermediate gel is a point of discussion.

In 1998, Temuujin et al.^{261,262} formed M–S–H by a mechanochemical process, rather than hydrothermal synthesis: $\text{Mg}(\text{OH})_2$, MgO, and silicic acid were combined in a high-energy grinding method to form gels, which were aged prior to analysis. The resulting M–S–H was reported to be a poorly crystalline mixture of talc- and chrysotile-like materials (as observed in the XRD patterns in Figure 11), similar to M–S–H produced hydrothermally.

There is also evidence that disordered M–S–H occurs naturally. Mitsuda²⁶³ discovered veins of M–S–H in association with 11-Å tobermorite from Heguri, Japan, believing it to be an intermediate product in the formation of talc. This

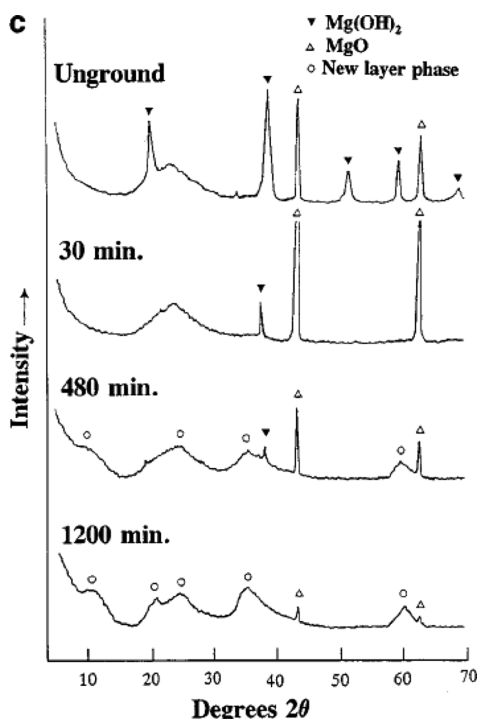


Figure 11. X-ray diffraction patterns of a MgO/silicic acid mixture ground for various times and then aged. The pattern labeled 1200 min displays a characteristic M–S–H diffraction pattern, which was identified by the authors of ref 262 as a “new layer phase”. Reproduced with permission from ref 262. Copyright 1998 Elsevier Ltd.

theory was further explored by Mitsuda and Taguchi in a study of hydrothermally produced M–S–H²⁶⁴ (up to 600 °C) until the poorly crystalline phase crystallized and transformed into talc. The formation of M–S–H in nature under hydrothermal conditions was also reported by Gunnarsson et al.,²⁶⁵ who noted the formation of poorly crystalline Mg silicate scale with an antigorite-like structure in geothermal installations in Iceland.

Focusing on M–S–H formation within cements, Brew and Glasser²¹⁸ undertook a study to synthesize and analyze M–S–H gels precipitated by the mixing of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$. Solid-state ^{29}Si NMR analysis of these gels revealed only slight structural differences as a function of Mg/Si ratio. These gels were also aged at 85 °C over 6 months, which resulted in structural changes, as the two highest-Mg gels (Mg/Si molar ratios of 0.89 and 0.94) developed different structural motifs upon aging compared to the lower-Mg gels, resulting in a shift in the position of the Q^3 peak in ^{29}Si MAS NMR spectra of the gels with higher Mg/Si ratios. This suggested the formation of a serpentine-like material at higher Mg content, whereas the lower Mg/Si gels more closely resembled a talc-like structure.

The precise nature of this serpentine-like material has until recently proven difficult to elucidate. The Mg-rich end of the serpentine group encompasses three minerals (antigorite, chrysotile, and lizardite), each polymorphs of $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$. Several studies have looked at the amorphized structure of these three minerals, which tend to be structurally very similar,^{266–269} so that the poorly crystalline mineral phases are difficult to differentiate from one another. Walling et al.²⁴² recently studied the structure of M–S–H cements derived from $\text{Mg}(\text{OH})_2$ and silica fume at a Mg/Si ratio of ~ 0.95 , and

through the application of ^{29}Si and ^{25}Mg solid-state NMR spectroscopies, found the structure of this gel to resemble poorly crystalline lizardite rather than an antigorite or talc-like assemblage, as depicted in Figure 12. A recent detailed study of

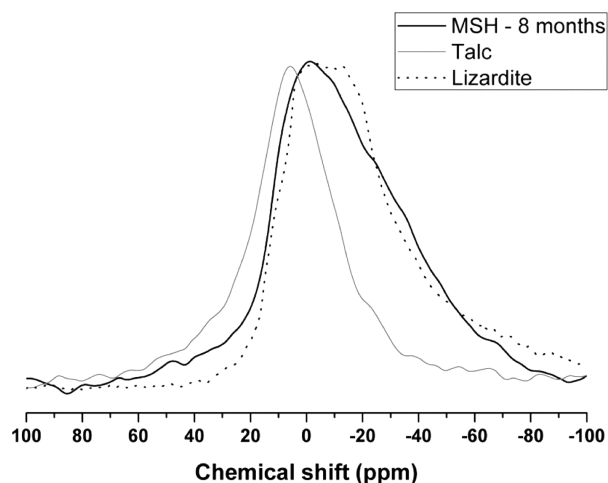


Figure 12. ^{25}Mg MAS NMR spectra of 8-month-cured M–S–H, talc, and lizardite. Adapted from ref 242.

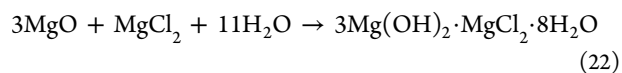
M–S–H and C–S–H gels by Lothenbach et al. noted the existence of M–S–H gels having Mg/Si ratios ranging from 0.7 to 1.3, with M–S–H and C–S–H forming separate gels with little probability of a solid solution between the two.²⁷⁰ This is complimented by the work of Roosz et al., who synthesized M–S–H with Mg/Si ratios of 0.57 and 1.07 and found the former gel to be structurally similar to 2:1 magnesium/silicon phyllosilicates.²¹⁷

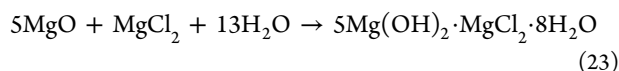
4.3. Conclusions

To date, no studies have described the scaleup of M–S–H for commercial cementing applications, and little work has been undertaken on the mechanical properties of M–S–H, other than compressive strength, or its long-term durability. As a cement, M–S–H appears to be restricted by its very slow setting at ambient temperatures, which might limit large-scale utilization in construction but which is likely to be somewhat less problematic in specific applications involving the immobilization and disposal of nuclear waste. The precise structural details of the gel phase(s) forming in M–S–H binder systems also remain to some extent unclear. The relatively high cost of highly reactive silica compared to PC means that, for the foreseeable future, it is likely that M–S–H will remain a niche cement unless more economical sources of silica can be utilized, with research likely instead focusing on M–S–H alteration products within PC-based cementitious systems. The potential for improvements in mechanochemical properties and reaction speeds are significant, however, and might possibly herald a brighter future for this cement through the application of an improved chemical- and microstructural-level understanding to the optimization of engineering properties.

5. MAGNESIUM OXYCHLORIDE (SOREL) CEMENTS

Magnesium oxychloride (MOC) cements are based on the aqueous reaction between MgO and MgCl_2 , for example





forming a variety of phases that are highly dependent on the precursor molar ratios, temperature and magnesium reactivity.

First reported by Sorel in a 1866 patent²⁷¹ and further elucidated in a widely recognized journal publication by the same author in 1867,²⁷² these cements initially proved popular because of their attractive, marble-like appearance. Binding phases corresponding to those formed in MOC cements can be synthesized through the dissolution of MgO in an aqueous solution of MgCl_2 , forming a homogeneous gel from which basic magnesium chloride salts precipitate. These salts are often expressed as $x\text{Mg}(\text{OH})_2 \cdot y\text{MgCl}_2 \cdot z\text{H}_2\text{O}$ or $x\text{MgO} \cdot y\text{MgCl}_2 \cdot (z + x)\text{H}_2\text{O}$, leading to the abbreviations “3 phase” and “5 phase”, derived from the ratio (x/y) of $\text{Mg}(\text{OH})_2$ to MgCl_2 in each phase.

The ability of MOC cements to bind and consolidate large quantities of diverse filler materials ranging from granite to sawdust, with good compressive and tensile strengths, has furthered their adoption. Historical uses ranged from ornamental applications (imitation ivory, billiard balls, door handles) to floors, stucco,²⁷³ grinding wheels,²⁷⁴ and even burial vaults.²⁷⁵ Various sources note widespread use as a wood substitute in flooring for ships from the early 1900s to the 1950s,^{276,277} including the RMS Olympic and RMS Titanic ocean liners,²⁷⁸ where fire resistance and acoustic damping properties were desired. However, the popularity of MOC cements has precipitously declined in the past half-century because of their poor water resistance and subsequent degradation during service.

Typically, MOC cement is made by first combining MgO, generated through the calcination of magnesite, with filler materials. This mixture is then packed into a shape, moistened with a solution of MgCl_2 (typically at a concentration of ~ 1.5 – 3 mol/L^{272,279}), and left to harden through eqs 22 and 23. The variation in reactivity of MgO due to different impurities and calcination temperatures, combined with differing concentrations of MgCl_2 solution, has resulted in considerable variability in the reaction products formed and, consequently, in the physical properties^{280,281} of the hardened cements. Heat, whether applied externally or generated during hydration, alters the phases formed,^{282,283} as does carbonation,²⁸⁴ further complicating the discussion of the precise binding phases present in hardened MOC cements.

Although discussed here as a cementing system in its own right, magnesium oxychloride phases have also been found to exist as degradation products in high-alumina cements and PCs as a result of chloride attack.^{285,286}

5.1. Phase Composition

Early attempts to determine the composition of the MOC binding phase began with a series of experiments by Bender in 1871,²⁸⁷ who concluded that $5\text{MgO} \cdot \text{MgCl}_2 \cdot 17\text{H}_2\text{O}$ ($14\text{H}_2\text{O}$ when dried) was the binding phase formed, whereas, in 1873, Krause²⁸⁸ stated that $10\text{MgO} \cdot \text{MgCl}_2 \cdot 14\text{H}_2\text{O}$ was the binding phase. This disagreement was resolved by Robinson and Waggaman²⁸⁹ over 30 years later, who concluded that $3\text{MgO} \cdot \text{MgCl}_2 \cdot 10\text{H}_2\text{O}$ is the stable product formed in the MgO – HCl – H_2O system at 25°C when MgO is in excess.

The 3 phase was thus accepted as the key binding phase, supported by research by Paterson²⁷⁶ and Lukens,²⁹⁰ although reservations were stated regarding its actual water content. The crystalline water content of the 3 phase, and thus its full

chemical makeup, was determined as $3\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ by Walter-Lévy and de Wolff.^{291,292}

However, the 3 phase is not the only phase formed during the formation of MOC cements. A series of articles by Feitknecht^{293–295} from 1926 to 1930 analyzed the formation of MOC phases with varying MgCl_2 concentrations and postulated that various phases (including 3–1–10 and 5–1–10) were forming, based on the first optical micrographs of needle-like crystals of MOC phases (as shown in Figure 13)

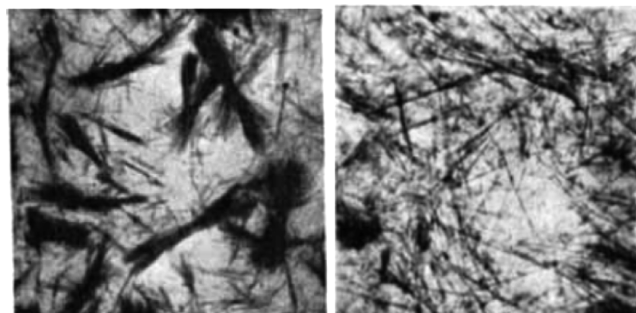


Figure 13. Optical micrographs of MOC phases precipitating from solution. Reproduced with permission from ref 293. Copyright 2004 John Wiley & Sons.

and X-ray diffraction patterns for these phases. In 1944, Feitknecht and Held again confirmed the existence of the 5 phase and revised the description of the crystalline water content within the composition to $5\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 7\text{H}_2\text{O}$,²⁹⁶ which is now known as the 5 phase.

The formation of these two phases (3 phase and 5 phase) was reviewed by Walter-Lévy²⁹² in 1949, who noted that the 5 phase formed principally in solutions containing >1.5 M MgCl_2 , although the excess MgCl_2 in solution gradually transformed the 5 phase to the 3 phase, whereas the use of MgCl_2 solutions with concentrations of <1.5 M instead yielded $\text{Mg}(\text{OH})_2$. The crystallographic details of these two phases were then accurately analyzed for the first time by de Wolff and Walter-Lévy,^{297,298} considering eight crystal-bound water molecules to be present in both the 3 and 5 phases, with the 3 phase found to be triclinic whereas the 5 phase was reported as monoclinic.

Much later, in 2007, Sugimoto et al.²⁹⁹ provided crystal structure descriptions for both the 3 and 5 phases. The 3 phase was described as consisting of two $\text{Mg}(\text{OH})_4(\text{OH}_2)_2$ octahedra, forming chains with Cl and H_2O intercalated between them, forming the $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O}$ crystal. The 5 phase consists of two $\text{Mg}(\text{OH})_4(\text{OH}_2)_2$ and one $\text{Mg}(\text{OH})_6$ octahedra, forming a triple chain, with disordered intercalated Cl and H_2O , forming the $\text{Mg}_3(\text{OH})_5\text{Cl} \cdot 4\text{H}_2\text{O}$ crystal. Both crystal structures are displayed in Figure 14, along with that of the chlorocarbonate phase.

Another complicated and disputed matter is the proposed carbonation of MOC phases. The chlorocarbonate phase (sometimes called “chlorartinite”), was noted by Walter-Lévy²⁹¹ and defined by de Wolff and Walter-Lévy²⁹⁷ as $\text{Mg}_2(\text{OH})\text{Cl} \cdot \text{CO}_3 \cdot 3\text{H}_2\text{O}$. This was much later clarified by Sugimoto et al. in 2006,³⁰⁰ where chlorartinite was found to have a structure entirely different from that of artinite $\{[\text{Mg}_2(\text{CO}_3)(\text{OH})_2] \cdot 3\text{H}_2\text{O}$ with Mg octahedra in zigzag double chains} and was instead refined as $[\text{Mg}_2(\text{CO}_3)(\text{H}_2\text{O})(\text{OH})]\text{Cl} \cdot \text{H}_2\text{O}$ with Mg octahedra in 15-membered puckered rings. The

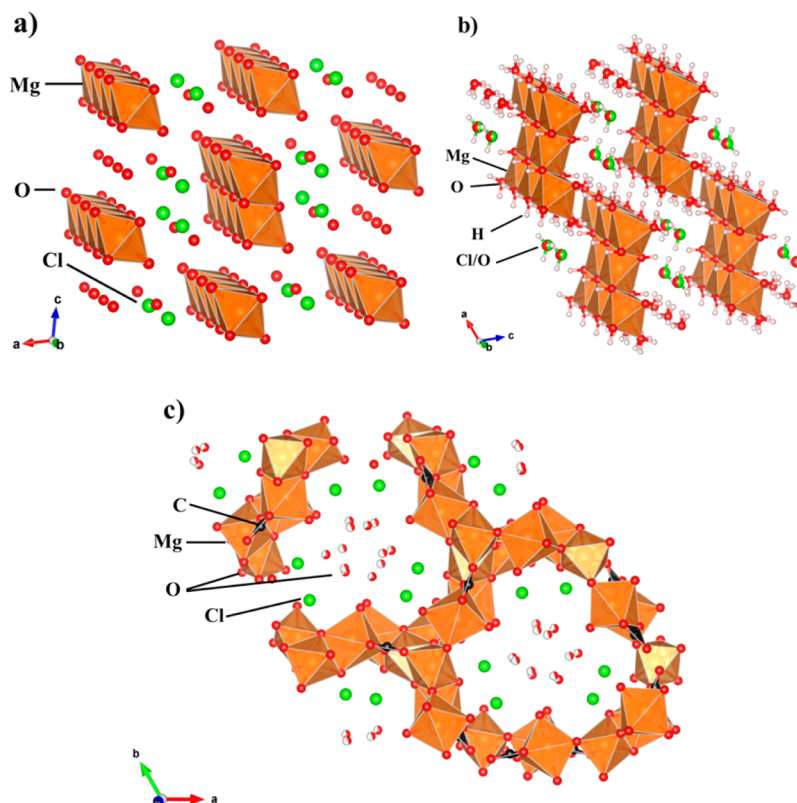


Figure 14. Crystal structures of the (a) 3 phase, (b) 5 phase, and (c) chlorocarbonate drawn from refs 298–300. (Note that the hydrogen positions are not defined in panels a and c.)

importance of this phase in practical applications of MOC cements is discussed in more detail in section 5.2.

The understanding of phase composition became yet more complicated when, in 1951, Walter-Lévy and Bianco³⁰¹ noted the appearance of two new phases that formed above 100 °C. These were characterized as 2–1–4 and 9–1–5, of which the 2 phase was not stable at room temperature, converting back to 3–1–8. The structure of the 9 phase was much later refined to 9–1–4 by Dinnebier et al.³⁰² Bianco²⁸³ performed an extended study of higher-temperature phases, from 50 to 175 °C, suggesting the additional formation of 2–1–2 and 3–1–1; because of the significant heat of hydration evolved during the initial setting and hardening of MOC cements, the phases formed at temperatures greater than 100 °C have the potential to form within large blocks of the cement, even when poured at room temperature. While studying the 9–1–4 phase, Dinnebier et al.³⁰² postulated that this phase existed only as an intermediate strength-giving phase that rapidly formed during MOC hydration and eventually transformed into the 3 phase (Figure 15). It was suggested that this was also true of the 5 phase, proposed to exist essentially as a metastable phase at room temperature, before stabilizing as the 3 phase.³⁰²

The potential formation of these higher-temperature phases was particularly highlighted by Newman et al.,³⁰³ who studied the heat generation of MOCs using a formulation that was likely to generate the 5 phase (expected to be the most exothermic). The internal sample temperature reached 147 °C, with a deleterious effect on strength. This finding leads to a complicated situation where MOC monoliths can experience spatial variations in phase assemblages as a function of the temperatures experienced during curing, as the high-temper-

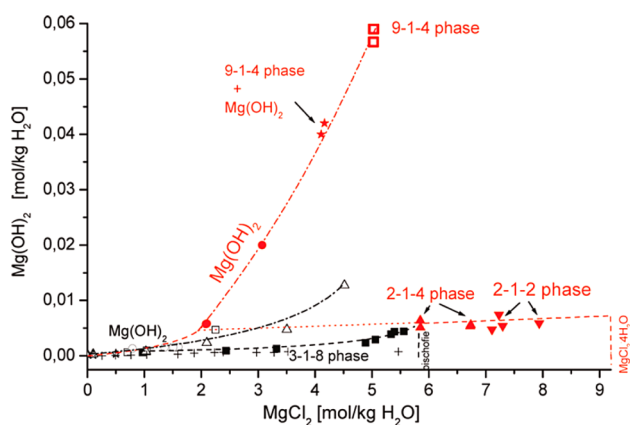


Figure 15. Phase equilibria at 120 °C (red) compared to literature data at 25 °C (black), as compiled by Dinnebier et al.³⁰² Reproduced with permission from ref 302. Copyright 2010 American Chemical Society.

ature phases tend to persist for some time at room temperature upon cooling.

The thermal stability of the then-known MOC phases was analyzed by Cole and Demediuk in a 1955 thermogravimetric (TG)/differential thermal analysis (DTA) study.²⁸⁴ Heating yielded a variety of stable hydrate forms of each phase, formed through stepwise dehydration (Figure 16). The proposed stable hydrate forms of each phase were as follows:

- 2 phase: 4H₂O, 2H₂O, anhydrous
- 3 phase: 8H₂O, 5H₂O, 4H₂O, anhydrous
- 5 phase: 8H₂O, 5 or 4H₂O, 3H₂O, anhydrous
- 9 phase: 5H₂O, 2H₂O, anhydrous

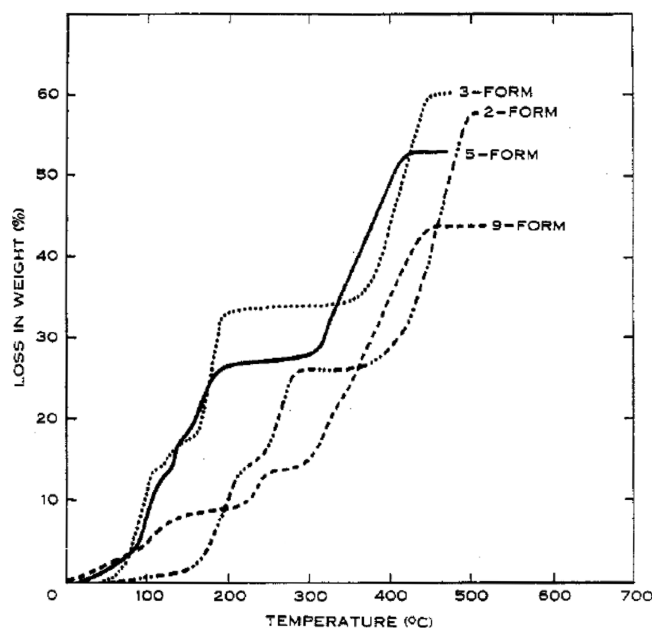


Figure 16. Thermogravimetric data for the 2, 3, 5, and 9 phases up to ~ 500 °C. Reproduced with permission from ref 284. Copyright 1955 CSIRO.

Among the dehydrated phases proposed by Cole and Demediuk,²⁸⁴ the lower hydrates of the 3 phase were again shown to form by Runčevski et al. in 2014, who observed and characterized 3–1–5.4 and 3–1–4.6 hydrates during synchrotron XRD and TG dehydration studies.³⁰⁴ The high-temperature 2–1–2 phase was confirmed in 2012 by Dinnebier et al.,²⁸² as a lower hydration state of 2–1–4 formed by in situ dehydration, with both phases forming as fine needles. These phases were both produced at elevated temperature in ~ 7 M MgCl_2 solutions, with lower concentrations resulting in 9–1–4 formation (as shown in Figure 17).²⁸² Phases that have been identified to date are listed in Table 6.

Based on the development of this crystallographic understanding of the phases formed, it has also become possible to design and manipulate the phase equilibria within MOC binders, particularly to improve the durability and/or strength of the cements. High strengths are typically achieved by maximizing the rapid formation of the 5 phase, where the interlocking crystalline needles of this phase have long been believed to be the source of strength.^{284,307} Matković and Young,³⁰⁸ however, suggested that needle interlocking was not the major source of strength, but rather that the needles formed in areas of porosity, which can result in the early stiffening of the paste. These authors stated that, once the voids are filled with crystallites, the MOC microstructure begins to densify, which was proposed to be responsible for the main strength gain.

In 1976, Sorrell and Armstrong published the first comprehensive phase diagram for MOC binders at room temperature,³⁰⁹ with formation of the 5 phase occurring in only a narrow window in the phase diagram. MOCs are unstable in the presence of excess water, breaking down into MgCl_2 and $\text{Mg}(\text{OH})_2$, and conversion to hydromagnesite $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$ can also result from chloride leaching.³⁰⁹ Unreacted MgCl_2 can migrate to the surface of a monolithic sample, leading to unsightly white deposits

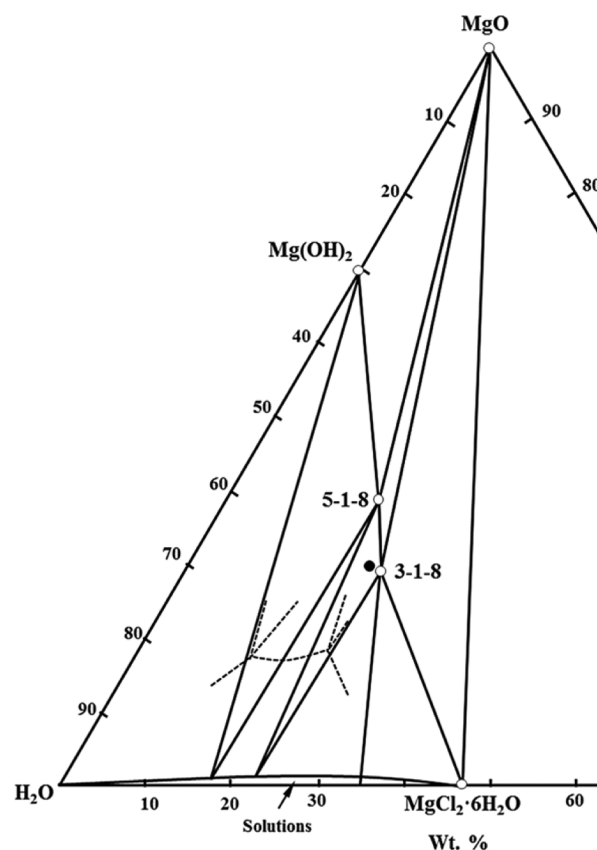


Figure 17. Phase diagram at 23 ± 3 °C of MgO – MgCl_2 – H_2O , drawn from the findings of Urwongse and Sorrell.³¹⁰ The composition marked with a solid black circle corresponds to the time-resolved analysis presented in Figure 18.

(efflorescence), and unreacted MgO can cause dimensional stability issues, further affecting the durability of these cements.

In 1980, Urwongse and Sorrell³¹⁰ published a key article on the solubility of MgO in HCl solutions at 23 °C that further refined the MgO – MgCl_2 – H_2O ternary diagram for a sealed system (Figure 17). They noted that, because of the tendency of the 5 phase to form more rapidly than the 3 phase (as in Figure 18), previous experimental studies that analyzed samples after a few days of reaction might have concluded that the 5 phase has a greater range of stability than is truly the case at equilibrium, as it is metastable with respect to the 3 phase under various conditions. Urwongse and Sorrell also noted that initial cement setting happens prior to evident crystallization of either the 3 or 5 phase and, therefore, that gel formation is crucial, suggesting that crystallization happens from a super-saturated solution; this might be related to an Ostwald step rule-like process. It was also noted that formulations aiming to produce the 3 phase react more slowly and have a greater tendency to form the less soluble chlorocarbonates than those dominated by the 5 phase.

Chau and Li^{281,311,312} studied the varying effects of molar ratios on the strength and phase development in MOC binders within the ternary MgO – MgCl_2 – H_2O system. These formulations were chosen to form MOC binders containing appreciable quantities of the 5 phase, to achieve void filling and early strength development. Very high strengths (up to 155 MPa) were achieved after 14 days of curing using excess MgO , leading the authors to state that this was required for a “good” cement. However, a dead-burned MgO was used, resulting in

Table 6. Phases Observed in Magnesium Oxychloride Cements

phase	composition	characterized by	powder diffraction file (PDF) card no.	$\Delta_f G_m^\circ$ (kJ mol ⁻¹)
3-1-8	3MgO·MgCl ₂ ·11H ₂ O 3Mg(OH) ₂ ·MgCl ₂ ·8H ₂ O	de Wolff and Walter-Lévy ^{297,298}	00-07-0412	-2552 ³⁰⁵
5-1-8	5MgO·MgCl ₂ ·13H ₂ O 5Mg(OH) ₂ ·MgCl ₂ ·8H ₂ O	de Wolff and Walter-Lévy ²⁹⁷ Sugimoto et al. ²⁹⁹	00-07-0420	-3385 ³⁰⁶
chlorocarbonate (chlorartinite)	Mg ₂ CO ₃ (OH)Cl·2H ₂ O (Sugimoto et al.)	de Wolff and Walter-Lévy ²⁹⁸	00-07-0278	—
	Mg ₂ CO ₃ (OH)Cl·3H ₂ O	Sugimoto et al. ³⁰⁰	00-50-1690	—
2-1-2	2Mg(OH) ₂ ·MgCl ₂ ·2H ₂ O	Dinnebier et al. ²⁸²	00-012-0133	—
2-1-4	2Mg(OH) ₂ ·MgCl ₂ ·4H ₂ O	Dinnebier et al. ²⁸²	00-012-0116	—
9-1-4	9Mg(OH) ₂ ·MgCl ₂ ·4H ₂ O	Dinnebier et al. ³⁰²	00-007-0409	—

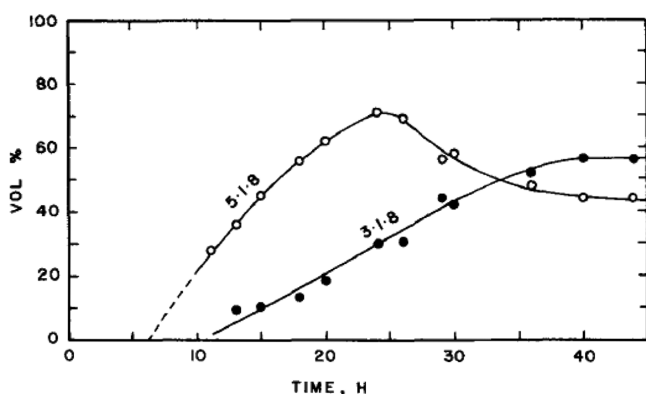


Figure 18. Relative amounts of 5-1-8 and 3-1-8 phases as a function of time, in the composition marked with a solid black circle in Figure 17. Reproduced with permission from ref 310. Copyright 2006 John Wiley & Sons.

nonequilibrium conditions because of the presence of remnant MgO. The authors stated that “excess or unconsumed MgO powder acts as a filler...”; however, care should be taken, as unreacted MgO can cause serious unsoundness (dimensional instability) in cements because of its slow hydration to Mg(OH)₂, which occupies a substantially larger volume.³¹³ It should thus be carefully considered whether the optimum formulation for MOC binders should contain substantial quantities of unreacted dead-burned MgO.

5.2. Chlorocarbonate: Relation to Strength and Durability

The tendency of the 3 phase to transform into a chlorocarbonate phase [Mg(OH)₂·MgCl₂·2MgCO₃·6H₂O] when exposed to ambient air^{284,310} and the relationship of this process to strength and durability raise important questions regarding the in-service properties of MOC cements. There are tentative indications that the formation of chlorocarbonate is welcome because of the lower solubility of this phase compared to the oxychloride phases, thus forming a semiprotective skin on top of the MOC cement.³⁰⁹ This indicates that such a process might be desirable for external applications, especially when the material is used as a stucco; however, few studies exist on the protective (or otherwise) nature of this phase.

Of these few studies, however, those that focus on the application of MOC cements during the restoration of the Acropolis site in Athens are particularly insightful. MOC cements (also called “Meyer stone glue” in Greece) were used during the restoration of the Erechtheion temple, partly because of the marble-like appearance achieved, during the 1970s. However, the subsequent degradation of the MOC has caused substantial damage to the Pentelic marble^{314,315} as a

result of staining and expansion. In 1999, Maravelaki-Kalaitzaki and Moraitou³¹⁶ studied some of these mortars and noted that, in line with the literature, mortars exposed to water were destabilized, dissociating to Mg(OH)₂ and MgCl₂ in solution with associated loss of strength. Although the chlorocarbonate phase could reduce leaching, its formation caused a large volume change that induced cracking in the surrounding marble, causing considerable damage. This corroborates an earlier study by Castellar et al.,³¹⁷ who found cracks in MOC polishing bricks that they assigned to dimensional changes during carbonation. Maravelaki-Kalaitzaki and Moraitou also noted the presence of hydromagnesite in leached, carbonated mortars, potentially as a degradation product of chlorocarbonate.³¹⁶

The effect of chlorartinite (magnesium chlorocarbonate) on MOC durability was clarified somewhat in 2006, when Sugimoto et al.³⁰⁰ found that, although the presence of chlorartinite was not damaging per se, this phase can rapidly exchange water with the environment. In particular, crystal water was lost simply through exposure to an inert gas atmosphere at room temperature, accompanied by a density change of >15%. This makes MOC binders containing chlorartinite highly susceptible to changes in humidity, with potential for associated cracking, and suggests that the chlorocarbonate phase is not as protective as has been proposed, especially if the cement is exposed to wide variations in humidity, as in an external service environment.

5.3. Influence of MgO Calcination

The effects of MgO reactivity and, therefore, the conditions of magnesite calcination are crucial in defining MOC formation. Calcination for longer durations and at higher temperatures produces a less reactive MgO (i.e., “dead-burned”),¹⁷ as noted in section 1.2. These effects were noted in the work of Harper,²⁷⁹ who showed that increased calcination temperatures and various impurities delay the setting and exothermic events in MOC pastes. This significant retardation highlights the need for careful control and characterization of the MgO used in the production of MOC binders.

These findings were echoed by Bilinski and Alegret,^{318,319} who observed that the setting times and strengths of MOC cements varied widely as a function of MgO calcination conditions. The calcination conditions can influence water demand (because of surface area), therefore affecting the ionic strength of the MgCl₂ solution used to achieve a binder with a given Mg/Cl ratio and, thus, the phase formation. Generally, cements produced using magnesite calcined at 800–1000 °C produced substantially stronger cements than those calcined at less than 800 °C,^{279,320} with reports of up to a factor of 10

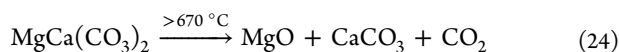
increase in strength when compared to MgO calcined at 600 to 1000 °C.²⁷⁹

5.4. Cost-Effective Production

In 1922, Shaw and Bole²⁷³ noted that the high production costs and frequent cracking and buckling of MOC floors were significant disadvantages restricting MOC uptake at that time. The latter can now be better controlled because of the improved understanding of phase equilibria in the MOC system, but the former continues to be a problem. Attempts have been made to make use of locally available substitutes to reduce costs, including the use of bittern water (solutions left after sodium chloride precipitation from brines) instead of pure MgCl₂ solutions.³²¹ This has led to numerous regional revivals of MOC binders in areas where brines are abundant, especially around Salt Lake City, UT,^{322,323} and as evidenced by current research by the Qinghai Institute of Salt Lakes, Qinghai, China.^{281,324–326}

Alongside the availability of MgCl₂, the lack of widely distributed high-grade magnesite deposits has also historically severely hampered the adoption of MOC binders. This has resulted in several studies of the use of dolomite [CaMg(CO₃)₂] instead of magnesite for economic reasons,^{327,328} as the former is much more widely distributed and easily available.²⁷³ Several early patents claimed that dolomite could be used to produce MOC binders if the dolomite was carefully calcined by controlling CO₂ pressure and firing at ~750 °C to produce MgO and CaCO₃.^{327–330}

Typically, the thermal decomposition of dolomite is reported as a two-stage decomposition, with the reaction



yielding MgO and CaCO₃, followed by CaCO₃ decomposition at higher temperature according to eq 10.³³¹

These reactions often merge into an apparently single-step process in air,³³¹ and varying decomposition temperatures have been reported depending on mineral purity and decomposition conditions,^{328,332,333} posing difficulties for CaO-free production of MgO. This is illustrated in the combined thermal analysis/XRD study undertaken by MacKenzie and Meinhold³³¹ (Figure 19), who reported that CaO begins to form very shortly after MgO is detected within the samples.

If, however, the partial pressure of CO₂ is increased, the resulting decomposition regions can be separated.³³² The initial decomposition associated with MgO formation can occur at a lower temperature (fully decomposing by ~800 °C), whereas CaCO₃ decomposition is pushed to a higher temperature, ~950 °C. McIntosh et al.³²⁹ illustrated this approach (Figure 20), undertaking DTA on dolomite under flowing N₂ and then incrementally increasing the atmospheric concentration of CO₂ to 100%. This clearly separates the constituent peaks,³³⁴ which enables the production of MgO without CaO coformation.

The presence of impurities in dolomite has been shown to severely affect its reaction and usability as a source of MgO,³³⁵ and the avoidance of free CaO formation is imperative, as even as little as 2 wt % of this impurity is detrimental to the service life of MOC binders.³²⁸

Other attempts to improve MOC binders include coformation of other oxychloride salts. Cations with a charge and crystal ionic radius similar to those of VI-coordinated Mg²⁺ (0.86 Å), such as Zn²⁺ (0.88 Å) and Cu²⁺ (0.87 Å),³³⁶ can also form oxychloride binders, as described for the first time in the patent literature in 1872, where MOC cements with partial or

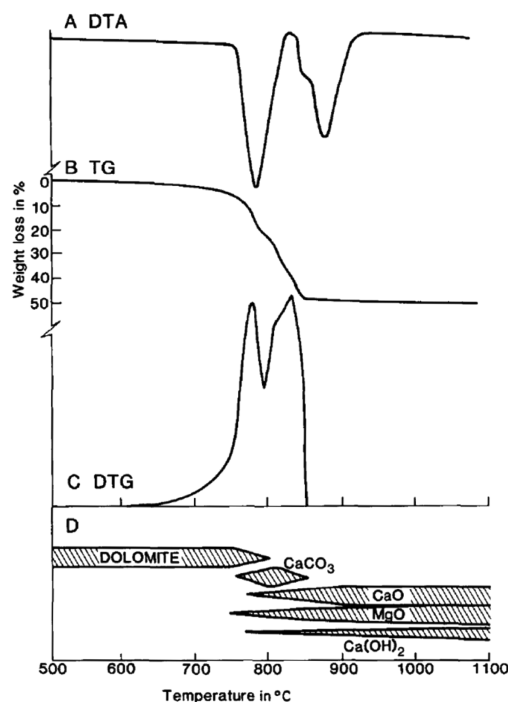


Figure 19. Thermal analysis of dolomite, including (D) semischematic X-ray phase compositions. (A) DTA was undertaken in a static autogenous atmosphere, whereas (B,C) TG/DTG was performed in flowing Ar, resulting in differences in the decomposition temperatures between the techniques. Reproduced with permission from ref 331. Copyright 1993 Elsevier Ltd.

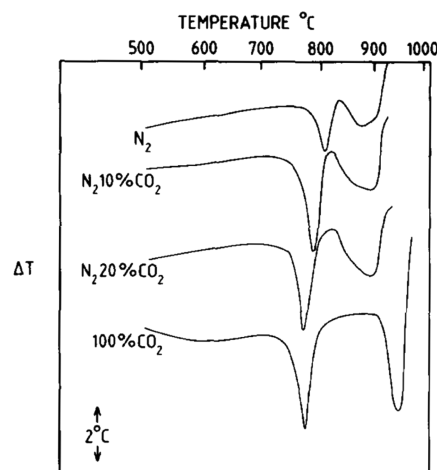


Figure 20. DTA curves for the calcination of dolomite in varying atmospheres ranging from pure N₂ to pure CO₂. Reproduced with permission from ref 334. Copyright 1990 Elsevier Ltd.

full replacement of MgO with ZnO were used for the production of various articles.^{337–339} The zinc oxychloride system was later characterized by Sorrell³⁴⁰ and was observed to form 4–1–5 and 1–1–2 phases, the latter of which is unstable in water.

In 1937 Hubbell added finely divided copper to MOC binders, forming cupric oxychloride and atacamite (3CuO·CuCl₂·3H₂O).^{341,342} This was claimed to increase strength, reduce solubility and reduce efflorescence of the excess MgCl₂. Various patents by Hubbell described the use of additions of finely divided copper metal or copper oxide,^{343–345} while

copper sulfate and carbonate were later used by Whitehead.³⁴⁶ Farrell and Wolff³⁴⁷ demonstrated the antiseptic properties of these materials, and this characteristic is now exploited in the use of cupric oxychloride-containing flooring materials for commercial kitchens and work surfaces.³⁴⁸

5.5. Water Resistance

Another principal reason for the decline in use of MOC binders has been the susceptibility of these materials to deleterious processes induced by exposure to moisture.²⁸⁹ In moist conditions, the binding phases dissolve into a solution of $\text{Mg}(\text{OH})_2$ and MgCl_2 , resulting in the loss of the strength of the cement. Zhou et al.³⁴⁹ calculated that the 3 phase is unstable in a solution with a Mg molality of <2.25 mol/kg, whereas the 5 phase is unstable for Mg molalities of 1.47 mol/kg. Additionally, the release of MgCl_2 is particularly unwelcome near any structures containing steel reinforcing because of the risk of the chlorides causing significant steel corrosion. Additions of “waterproofing” fillers have ranged from paraffin-soaked sawdust³³⁰ and Solvay process residues³⁵⁰ at the turn of the 20th century to amorphous silica³⁵¹ and, more recently, coal fly ash.^{326,352} Melamine formaldehyde,³⁵³ latex (combined with glass fibers), and other polymers^{354,355} have also both been used to shield MOC phases from water.

A promising development illustrated by several articles is the use of small quantities of phosphates to improve the stability of MOC phases. This ability was claimed by Stewart in 1932;³⁵⁶ however, little substantial literature existed until the 21st century. Deng³⁵⁷ investigated the effects of small phosphate additions [up to 1.7 wt % phosphoric acid, NaH_2PO_4 , or $(\text{NH}_4)_2\text{H}_2\text{PO}_4$] on the properties of MOC binders during immersion in water for 60 days. Phosphates were found to greatly improve compressive strength retention: Up to 96% of the dry-cured strength was retained when 0.74 wt % H_3PO_4 was added, compared to 6.4% retention for the unmodified MOC. This was not attributed to the formation of insoluble magnesium phosphates; rather, it was observed that the phosphates reduced the level of free Mg^{2+} ions required in solution and, thus, stabilized the 5 phase.^{357,358} This was confirmed by Zhou et al., who found that a 0.5 wt % addition of NaH_2PO_4 altered the conditions of phase formation in MOC cements, promoting the formation of the 5 phase and $\text{Mg}(\text{OH})_2$,³⁴⁹ as demonstrated in Figure 21, where the phase boundaries are altered when phosphate is added. However, the precise mechanisms involved in the enhancement of the water resistance of MOC cements by the addition of phosphate require substantial further research.

5.6. Current Uses for MOC Cements

In the past decades, MOC binders have become less popular as flooring and stucco materials because of the issues related to their susceptibility to water damage and their high costs compared to those water-resistant PCs or gypsum plasters, which are similarly susceptible to water damage but usually less expensive. Nonetheless, there is continuing interest related to the fire resistance of MOC cements, with particular interest in their use as a paintable substrate or internal plasterboard replacement. It is postulated that the large amount of crystalline water (typically $\sim 35\%$ hydrated water by weight) in MOC phases, which requires a large amount of energy to liberate, combined with the ability of MgO to effectively reflect heat gives MOC binders good heat resistance.³⁵⁹ Both the 3 and 5 phases decompose through stepwise dehydration, followed by dissociation and degradation to MgO and HCl by 600°C ;³²⁵

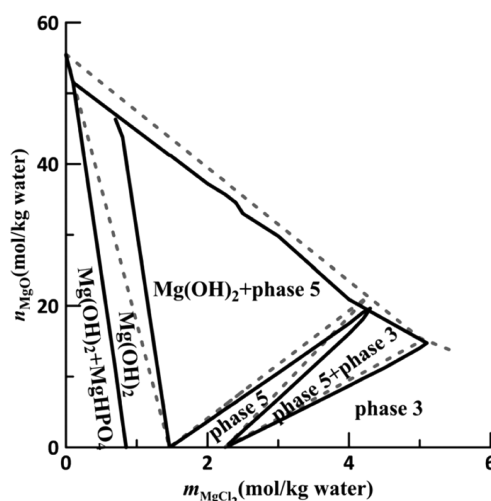


Figure 21. MgO – MgCl_2 – H_2O equilibrium phase diagram with 0.5% NaH_2PO_4 at 25°C and 0.1 MPa, with the phosphate-free diagram represented by dotted lines. Edited and reproduced with permission from ref 349. Copyright 2015 Elsevier Ltd.

this release of HCl upon heating must be considered as a point of caution related to the use of MOC binders for fire protection in domestic applications.

The ability of MOC cements to incorporate wood filler was exploited to produce “woodstone” panels, which have the appearance of chipboard and the ability to hold screws and nails but are fire-resistant.^{360,361} Closely related are “magnesium oxide boards”, which are often MOC blended with perlite and are used to replace plaster boards.^{362–364} Although fire-resistant, these boards are often marketed as carbon-neutral or “eco” products, because of the use of MgO and the low temperatures used in production. Although MgO is not an eco-material per se, a reduction in the heat required to form these boards has the potential to offer energy savings. Alongside wood fillers, the lower alkalinity of MOC cements compared to PCs also enables the incorporation of glass fiber reinforcement. Several patents exploit this characteristic to produce reinforced cement boards.^{365–367}

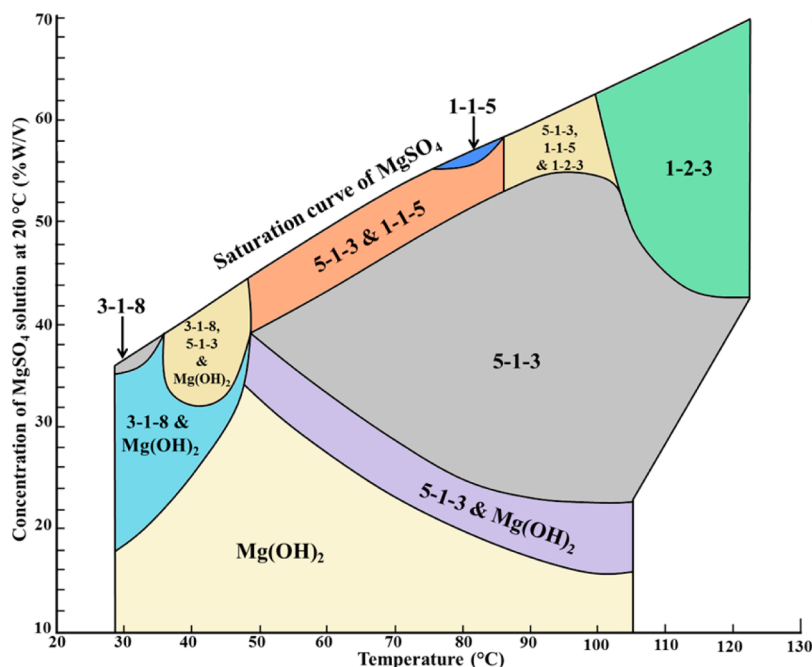
Several niche industrial applications for MOC cements also exist, such as temporary oil-well cements, accommodating varying additives, which are acid-soluble when the need for their removal arises;^{368–371} rock salt and potash mining to seal brine intrusions;^{302,372,373} and stabilization of nuclear waste repositories hosted in salt mines. Specifically, MOC cements are currently being used in the Asse II geological repository in Germany, where saline intrusions and instability require the use of a highly salt-tolerant cement.^{374,375} MOC cements are also proposed for use in a future high-level waste repository in a salt dome in Gorleben, Germany.^{376,377}

5.7. Conclusions

Beyond the technical uses noted in section 5.6 and applications in wall-board production, there is probably little prospect for a large-scale resurgence of MOC binders. The continuing complexity associated with ensuring a well-developed binding system, combined with the inherent instability and solubility issues of the major phases when in contact with water, will continue to limit their applicability. In wall-board applications, the market is more accustomed to gypsum-based products, which are produced on a much larger scale and at a lower cost in many countries. Carefully quality-controlled production and

Table 7. Phases Observed in Magnesium Oxysulfate Cements

phase	composition	most detailed crystallographic characterization	PDF card no.
3-1-8	$3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 8\text{H}_2\text{O}$	Dinnebier et al. ³⁸⁶	00-07-0418
5-1-3 (or 5-1-2)	$5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ [or $5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 2\text{H}_2\text{O}$]	Demediuk and Cole ³⁸⁷	00-07-0415
1-1-5	$\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 5\text{H}_2\text{O}$	Demediuk and Cole ³⁸⁷	00-13-0341
1-2-3	$\text{Mg}(\text{OH})_2 \cdot 2\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$	Demediuk and Cole ³⁸⁷	00-13-0349
5-1-7	$5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Runčevski et al. ³⁸⁸	

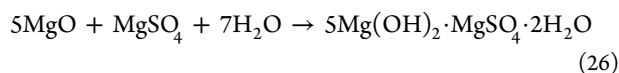
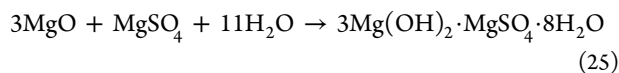
Figure 22. Phase equilibria in the system $\text{MgO-MgSO}_4\text{-H}_2\text{O}$. Redrawn from ref 387.

blending of a just-add-water MgO-MgCl_2 mixture at an industrial plant can certainly lead to the production of a viable cement for the production of precast items; however, the deliquescent nature of MgCl_2 severely affects the ability to store and market such a cement. MOC cements are, therefore, likely to remain a niche product for specialized applications, other than in areas where magnesium salts are very inexpensive and where they can offer cost savings compared to gypsum.

6. MAGNESIUM OXYSULFATE CEMENTS

6.1. Phase Composition

Magnesium oxysulfate (MOS) cements are similar in concept to MOC cements, except that MgSO_4 is used instead of MgCl_2 . A similar nomenclature scheme is applied to the $x\text{Mg}(\text{OH})_2 \cdot y\text{MgSO}_4 \cdot z\text{H}_2\text{O}$ phases, which are thus described analogously as the 3 phase, 5 phase, and so on; however, these phases are not isostructural to those formed in oxychloride cements that share the same names. Typically, formation will follow the equations



(the latter if heated), although several other phases can also be formed.

The history of these cements began with a patent granted in 1891 to Enricht for “Artificial stone or cement”,³⁷⁸ which

specified a combination of magnesium oxide, magnesium sulfate, and water that “forms an oxysulphate [sic] of magnesium, which on drying becomes a very hard cement or stone”. This was quickly followed by a similar 1892 patent, which included egg albumen and claimed to form a cement that was not attacked by the climate.³⁷⁹

MOS cements gained interest because of the less hygroscopic nature of magnesium sulfate compared to magnesium chloride^{356,380,381} and, hence, a claimed superior resistance to weathering.³⁸² This enabled easier shipping and a longer shelf life for bagged cements. These cements, however, find fewer applications, and consequently, there is much less literature available compared to MOC cements. MOS cements are more difficult to form because of the limited solubility of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ at room temperature, but the development of these materials based on sulfates does avoid the use of chlorides, making them significantly less damaging to steel reinforcing, although they still suffer from poor water resistance.

In 1892, Thugutt undertook a study on basic sulfates of magnesium and zinc,³⁸³ reporting the formation of $6\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$, but little further literature emerged until the 1930s, when Walter-Lévy³⁸⁴ studied the formation of carbonated magnesium sulfates. This work entailed additions of potassium carbonate or bicarbonate to a concentrated solution of magnesium sulfate, yielding $\text{Mg}_4(\text{OH})_2(\text{CO}_3)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, which reverted to an oxysulfate over time. The authors identified in particular the formation of $3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 8\text{H}_2\text{O}$ (the 3-1-8 MOS phase),³⁸⁵ later characterized in crystallographic detail by Dinnebier et al.³⁸⁶

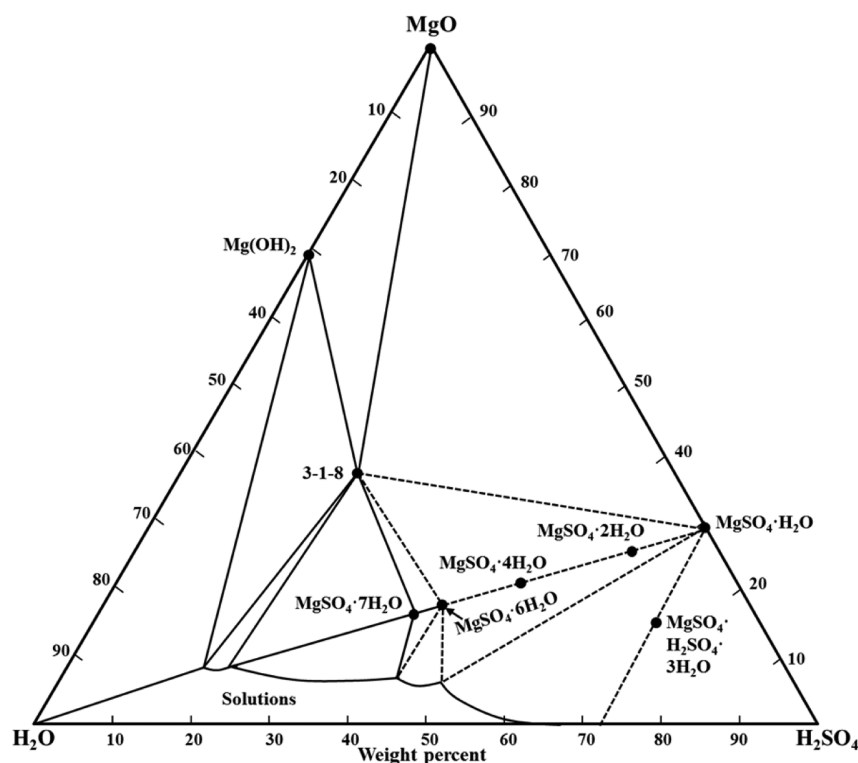


Figure 23. Phase diagram for the system $\text{MgO-H}_2\text{SO}_4\text{-H}_2\text{O}$ at 23 ± 3 °C. Drawn from ref 389.

In 1957, Demediuk and Cole³⁸⁷ undertook a comprehensive study of the $\text{MgO-MgSO}_4\text{-H}_2\text{O}$ system by analyzing precipitates from saturated solutions of MgSO_4 to which MgO was added, at temperatures from 30 to 120 °C. They identified four magnesium oxysulfate phases (3–1–8, 5–1–3, 1–1–5, and 1–2–3), which are among the known MOS phases detailed in Table 7.

The formation of these phases is strongly influenced by temperature, as is the solubility of MgSO_4 , which greatly increases with temperature. This increases the concentration of MgSO_4 in solution, enabling the precipitation of the 1–1–5 and 1–2–3 phases, which contain higher proportions of MgSO_4 . The construction of a phase diagram (Figure 22) identified several conditions under which pure phases could precipitate, as well as many mixed-phase areas,³⁸² although the as-drawn shapes of the boundaries of some of the regions identified do appear to be unusual in a thermodynamic sense.

Of particular interest is the existence of a single-phase Mg(OH)_2 region at low concentrations of MgSO_4 , conclusively showing that MOS phases are not water-resistant. The degree of instability depends on temperature, reaching a maximum in solubility at ~ 47 °C.

Urwongse and Sorrell³⁸⁹ developed a ternary phase diagram for $\text{MgO-H}_2\text{SO}_4\text{-H}_2\text{O}$ at 23 °C (Figure 23), where H_2SO_4 was used instead of the MgSO_4 in Figure 22. It was determined that the 3–1–8 phase was the main phase formed under a broad range of conditions, along with Mg(OH)_2 and hydrated forms of MgSO_4 . The 1–1–5 phase was also observed, although it was metastable at 23 °C. It was postulated that, in commercial cements, the 5–1–3 phase is the most desirable in terms of strength development characteristics, but it was also noted that this phase can be formed as a stable phase only under steam-curing conditions.

The formation of only a limited number of stable phases at near-ambient temperature is in good agreement with the results published by Demediuk and Cole,³⁸⁷ who observed only the 3 phase and Mg(OH)_2 at 30 °C (Figure 22). The 5 phase exists alone in a stable range between 50 and 120 °C, with a peak in stability at 100 °C, and in combination with the 3 phase and Mg(OH)_2 at 40 °C. Given the wide range of phases formed at elevated temperatures, there is a clear need for further ternary studies at temperatures up to 120 °C.

More recently, Dinnebier et al.,³⁸⁶ Runčevski et al.,³⁸⁸ and Wu et al.³⁹⁰ revisited the field of MOS cements with modern analytical techniques. Dinnebier et al.³⁸⁶ carried out equilibrium experiments in the MOS system, from which it was concluded that the 3–1–8 phase was unstable at room temperature, with the 5–1–2 phase reported as being the most stable. The 3–1–8 phase was found to form from a solution supersaturated in Mg^{2+} , whereas the 5–1–2 phase could be induced to form from an undersaturated solution through equilibration of a MgSO_4 solution with 3–1–8 precipitates (Figure 24). This suggests that the 3–1–8 phase is actually a metastable phase at room temperature, not the final stable product as previously believed. Those authors also undertook detailed high-resolution synchrotron X-ray diffraction characterization of the 3–1–8 phase, refining its structure (Table 7). It was also determined that the 5–1–3 and 5–1–2 phases were essentially the same structure, with 5–1–2 being a more correct description of the basic chemistry of this phase. Scanning electron micrographs of 5–1–2 and 3–1–8 crystals showed that the former consists of long needles, whereas the 3–1–8 phase forms flaky crystals. This interlocking needle-like structure (as previously discussed in section 5) and its space-filling properties are now understood to be the reasons why the 5–1–*n* phase is preferred for strength gain in industrial applications.

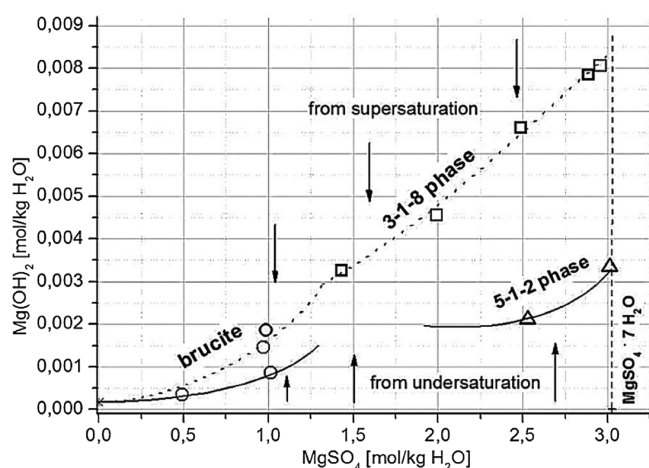


Figure 24. Solubility diagram at 25 °C for the MOS system. Reproduced with permission from ref 386. Copyright 2013 John Wiley & Sons.

Wu et al.³⁹⁰ reported the effects of phosphate additives in MOS cements at 23 °C and postulated that a 5–1–7 phase formed from high levels of MgO when phosphates were added to an MOS system. The approach used in that study differed from most of the MOS literature, as very high levels of MgO were used, whereas it is typical in most studies to slowly add MgO into solutions of MgSO₄ and investigate the precipitated phases. However, the MgO used by Wu et al. was only 80% pure, and the impact of impurities on the results is not known. This article was followed by crystallographic analysis of the 5–1–7 phase,³⁸⁸ which showed the formation of needle-like crystals. It was claimed that the new 5–1–7 phase could be produced by adding quantities of MgSO₄·7H₂O to water, then adding MgO and citric acid, and curing at 20 °C for a week. However, there has not yet been confirmation of the thermodynamic stability of this phase, which would enable it to be incorporated into the phase diagram of the system, and the fact that additives (phosphate or citric acid) seem to be required for its synthesis indicate that it is likely to be a metastable rather than stable phase.

6.2. Hydrothermal Production of Magnesium Oxysulfates

The temperature-dependent solubility of MgSO₄ has been shown to result in the formation of different phases, which has been studied in cements up to 120 °C.³⁸⁷ The formation of MOS phases at higher temperatures has been reported, especially around hydrothermal vents on ocean floors, where it was discovered that the heating of seawater to 325 °C resulted in MOS phase precipitation.³⁹¹ This was followed by numerous studies on varying MOS phases found around hydrothermal vents (and therefore exposed to higher temperatures and/or pressure) or from heating seawater compositions, including 1–3–1,³⁹² 5–1–4,³⁹³ 2–1–0,³⁹⁴ 1–2–2,³⁹⁵ and caminite (2–5–1).³⁹⁶ Although none of these phases have been used for cementitious purposes, their existence demonstrates the potential to push the MOS system beyond the limit of saturated steam curing. Also related to these topics are various articles on the hydrothermal preparation of magnesium oxysulfate whiskers, for use as precursors for MgO nanowires through in situ thermal decomposition, resulting in the formation of the 5–1–2/5–1–3 phase at temperatures of up to ~200 °C.^{397–400}

6.3. Current Uses for MOS

The use and analysis of MOS cements in the past 50 years have been largely confined to patent applications, with many patents describing the use of oxysulfate binders in the production of steam-cured panels or sheets, where steam curing is applied to reduce the solubility of MgSO₄ by favoring the formation of more MgO-rich hydrates and also to accelerate strength development. The earliest of these was by Biefeld in 1955,⁴⁰¹ who patented a method of producing MOS structural sheets, heating them to 77 °C to form a strong product. This patent also makes use of the lower pH of MOS compared to PC to enable the use of glass fiber reinforcement, as is also done in MOC systems. Pressurized steam at temperatures of up to 121 °C can also be used to form 5–1–3 phase cubes⁴⁰² with a curing time of less than 20 min, to enable rapid production of potentially commercially viable products.

6.4. Conclusions

Magnesium oxysulfate cements are extremely niche products, although, at present, there are very few applications that utilize MOS as a modern cementitious material. These materials appear to suffer from the same susceptibility to water as MOC binders and are therefore not useful as structural cements. The low solubility of MgSO₄ necessitates steam curing to produce many of the phases. This quite possibly limits MOS cement usage to internal boards or faux-wood panels that can be quickly produced, as well as sprayable fireproof coatings. However, in this instance, there are few obvious benefits over the use alternative existing commercial products, such as gypsum-based internal boards.

7. PERSPECTIVES: WHAT IS THE FUTURE OF MG-BASED CEMENTS?

The outlook for magnesium-based cements is one of cautious optimism. In their various guises, these cements are sometimes raised on pedestals as potential saviors of the built environment in the 21st century, but generally without appreciation of their inherent physical and economic limitations. These cements will continue to find a place in niche applications, where PC is unsuitable because of required physical or chemical properties. Magnesium phosphate cements have applications in environments requiring near-neutral-pH cements and for rapid repair, especially in cold environments. Magnesium silicate cements will likely be hindered by a lack of commercially viable sources of reactive silica, unless coupled with carbonate cements in a multiphase binder. These are also very technically immature, with fundamental physical properties of this binder yet to be understood. Large-scale reinforced concrete applications are unrealistic because of the inability of both magnesium phosphate and silicate cements to passivate mild steel, as well as the significant cost premium over well-established PC blends. Oxysalt-based cements are likely to remain very low-volume products because of poor water resistance, despite over 100 years of research. For dry internal applications, these cements compete against now well-established gypsum-based cements, such as plaster of Paris, with few benefits that justify the added complexity of producing a Sorel or oxysulfate cement binder.

Magnesium carbonate cements appear to hold the strongest prospect for the future, especially in lower-value precast applications such as blocks or tiles that can be produced and cured close to point-source emitters of CO₂ such as fossil-fuel power stations. These cements need to be properly formulated, however, with appreciation of magnesite calcination emissions

and the degree to which carbonation might occur throughout the material. CO₂ savings are possible through the use of these materials, especially if MgO can be produced from widely distributed magnesium silicate minerals; however, detailed life-cycle validation and optimization are required before they can truly be claimed to be carbon-neutral cements. Equally, durability testing is essential, as the long-term properties of most magnesium cements are unknown, reducing their appeal as modern building materials.

The global push for other alternative cements such as geopolymers, calcium sulfoaluminate (CSA) cements, and more ecofriendly blended optimized PC systems will provide strong competition against Mg cements. The future of the construction industry is likely to be one in which the norm becomes a suite or toolkit of cements tailored to specific applications, as Portland-based cements come under increasing environmental pressure. Magnesium-based cements can form part of this suite, but are unlikely to provide a magic bullet in terms of large-scale like-for-like replacement of PC in key construction applications. Nonetheless, the future of this class of cements does, on balance, appear promising.

8. CONCLUSIONS

This review has presented an overview of current and historical research and applications of MgO-based cements, including oxy-salt, silicate, phosphate, and carbonate systems. The manufacture and durability of these cements have been discussed in relation to their formulations and constituent materials. These cements occupy niche positions within industry today, but have in recent years gained increasing attention as solutions are being sought for the challenges facing the cement and construction industries in the 21st century. Although MgO cements have been researched for nearly 150 years, fundamental issues remain concerning their long-term durability and cost-effectiveness, especially regarding more recent additions to this family such as magnesium silicate and carbonate cements. Production of reinforced concrete or large-scale cast in situ construction work would seem to pose significant technical challenges across the class of MgO-based cements, but there are certainly smaller-scale applications involving the production of unreinforced elements under controlled conditions that are promising and approachable. However, care should be taken before MgO-based cements can be heralded as environmental saviors for the construction industry, as considerable research and development efforts are required before any of these cements could come close to providing a sustainable alternative binding system fit for large-scale use in the 21st century.

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John L. Provis is Professor of Cement Materials Science and Engineering and Head of the Engineering Graduate School at the University of Sheffield, U.K. He holds B.E. (Honours) (2002), B.Sc. (2002), and Ph.D. (2006) degrees from the University of Melbourne, Melbourne, Australia, and was awarded Dr.h.c. by Hasselt University, Hasselt, Belgium, in 2015. He is a Fellow of IOM³ and Chair of RILEM Technical Committee 247-DTA and has published more than 170 journal articles and book chapters related to novel and advanced cements.

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