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MgO-based cements – Current status and opportunities

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Abstract

The cement industry is a major contributor to the anthropogenic CO_2 emissions, with about 8% of all emissions coming from this sector. The global cement and concrete association has set a goal to achieve net-zero CO_2 concrete by 2050, with 45% of the reduction coming from alternatives to Portland cement, substitution, and carbon capture and utilization/storage (CCU/S) approaches. Magnesia-based cements offer a conceivable solution to this problem due to their potential for low-to-negative CO_2 emissions (CCU/S) but also being alternatives to Portland cement. The sources of magnesia can come from magnesium silicates or desalination brines which are carbon free for raw-material-related emissions (cf. carbonated rocks). This opens up possibilities for low or even net-negative carbon emissions. However, research on magnesia-based cements is still in its early stages.

In this paper, we summarize the current understanding of different MgO-based cements and their chemistries: magnesia oxysulfate cement, magnesia oxychloride cement, magnesia phosphate cement, magnesia carbonate cement, and magnesia silicate cement. We also discuss relevant research needed for MgO-based cements and concretes including the issues relating to the low pH of these cements and suitability of steel reinforcement. Alternatives reinforcements, suitable admixtures, and durability studies are the most needed for the further development of MgO-based concretes to achieve a radical CO_2 reduction in this industry. Additionally, techno-economic and life cycle assessments are also needed to assess the competition of raw materials and the produced binder or concrete with other solutions. Overall, magnesia-based cements are a promising emerging technology that requires further research and development to realize their potential in reducing CO_2 emissions in the construction industry.

Keywords: Magnesia-based cements; MgO supply; Low pH cements; Low-to-negative CO_2 emissions; carbon capture and utilization/storage (CCU/S); Magnesia oxysulfate cement; Magnesia oxychloride cement; Magnesia carbonate cement; Magnesia silicate cement

1 Introduction

The cement industry is responsible for approximately 8% of all anthropogenic CO_2 emissions, which consist mostly of hard-to-cut emissions related to the chemistry of the feedstocks. The Global Cement and Concrete Association (GCCA) has set an ambitious target to reach net-zero CO_2 concrete by the year 2050 [1], almost half of which (45%) is covered by Portland cement alternatives, substitution and carbon capture and utilization/storage (CCU/S) approaches.

Despite no sustainable production exists yet, magnesia-based cements have gained interest in concrete, but also in building products, repair materials, waste encapsulation and waste immobilisation applications due to their beneficial properties, including low pH, high strength, good surface finish, and potential for low-to-negative CO_2 emissions. Unlike CaO, magnesia can be sourced without raw-material-related CO_2 emissions from magnesium silicates or desalination brines, opening possibilities for net-negative carbon emissions. However, the research on many magnesia-based cements is still in its infancy. Nevertheless, magnesia-based solutions are rapidly gaining interest and different approaches are being scaled up globally.

The aim of this letter is to give a short introduction to magnesia-based cements, their potential, challenges and a general outlook for the field.

2 Supply chain of MgO

Currently MgO is commonly produced from the calcination of magnesite, $MgCO_3$, resulting in high amounts of CO_2 emissions (1.5 kg CO_2 per kg MgO produced vs. 0.786 kg CO_2

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per kg of CaO from $CaCO_3$) [2]. Global production of MgO is ~ 14 M tons annually [3] which includes both caustic calcined MgO and dead burned MgO. Dead burned MgO makes up > 60% of MgO production, primarily for refractory products, while caustic calcined MgO makes up the rest for applications in agriculture and construction. This number is obviously dwarfed by Portland cement (PC) production, which is on the order of several billions of tons annually. Therefore, paths to scale up sourcing and production in economically and environmentally friendly ways will be critical to make MgO-based cements a viable Portland cement alternative. The use of alternative feedstocks for MgO production is an active area of research as the current feedstock ($MgCO_3$) is not available in many parts of the world, therefore making producers overly reliant on imports.

2.1 MgO from desalination brine / seawater

Dissolved Mg^{2+} represents the fourth most abundant ion in the world's oceans [4], with a typical Mg^{2+} concentration of 52 mmol/L. In the wet process route, Mg hydroxide ($Mg(OH)_2$) is precipitated from Mg-rich brine or seawater and subsequently calcined to produce MgO. This is achieved via alkaline precipitation, in which an alkali (e.g. lime, sodium hydroxide) is added to elevate the pH to levels that cause Mg^{2+} to react with hydroxide ions (pH ~ 10.5) and form $Mg(OH)_2$ particles. There are also pre-treatment steps, e.g. acidification, that are needed, depending on the source. At the end of the this process, the $Mg(OH)_2$ slurry is passed through a filter, and the filter cake is calcined to produce MgO. It should be noted that the calcination of $Mg(OH)_2$ does not directly emit any CO_2 and is 17% less energy intensive than that of magnesite (excluding drying) [5, 6].

Currently the wet process route accounts for ~ 14 % of global MgO production. One major drawback that has limited widespread use is that compared to the current dry process route (i.e. calcination of magnesite), the wet process is highly energy intensive (17 vs 5.9 GJ per ton of MgO) [[7] via [8]]. Only regions that have low magnesite reserves but access to seawater/brine employ this process at meaningful scales (e.g., > 60% of Mg compounds produced annually in the U.S. are recovered from seawater/brine [9], while there are ongoing initiatives in the Middle East and Singapore to scale up MgO extraction from brines [10, 11]). Negative impacts on the environment of reject brine from desalination plants further motivate its conversion to construction products [12]. Still, it is currently not economically viable (nor appealing from a sustainability standpoint) to produce a cement based on this technology. However, with innovations in recovering minerals from seawater/brine [13] and renewable energy, it is expected that the wet process route will become increasingly more viable for wider applications in construction. For instance, seawater can be split into an alkaline and acidic stream via electrodialysis (ED) (Figure 1a) [14, 15]. While the alkaline stream drives $Mg(OH)_2$ precipitation, hydrochloric acid is also generated, which can be a high value co-product. If the electricity used to power the ED process is generated via renewable energy, it can be nearly carbon-free. One drawback is that these membranes are vulnerable to scaling. This requires pretreatment of the seawater, methods for scaling reduction, or eliminating the membrane altogether, e.g. membraneless electrolyzers (Figure 1b) [14, 16]. There are reported studies that utilize different alkali sources to drive $Mg(OH)_2$ precipitation [8], and assess the characteristics and performance of seawater/brine derived MgO-based cements [8, 17–19]. It was found that the alkali source impacts the properties of the formed MgO. The MgO derived via the wet process route (vs. dry) can exhibit higher purity and reactivity, thereby improving carbonation potential and resultant properties when used as cement [18]. Although still limited, the results of these studies are promising and motivate further investigation on MgO-based cements derived from seawater/brine.

2.2 MgO from Mg-Silicates

Ultramafic magnesium silicate minerals such as olivine ($(Mg,Fe)_2SiO_4$) could provide an almost endless supply of MgO, with estimated available worldwide reserves of over 10 trillion tonnes [20]. These ultramafic minerals are widely distributed across the world with major deposits in virtually all industrialized countries, as shown in Figure 1b. The potential use of olivine as a feedstock for cementitious construction materials has received considerable attention for many years, but primarily as a source for reactive silica to be used as a partial replacement for conventional Portland cement [21]. The recent interest in MgO recovery from magnesium silicate (MOMS) [2] such as olivine has been spurred by its potential use in carbon sequestration through the relatively rapid reaction between $Mg(OH)_2$ and CO_2 [22]. Many of the approaches being developed for carbon capture could be applied for the production of MgO to be used in magnesium cement systems.

There are essentially two major approaches to the recovery of MgO from magnesium silicate minerals: 1) acid leaching and, 2) alkaline dissolution [24]. There is a third method, in which olivine will react directly with water through the process of serpentinization [25], which results in the formation of the mineral serpentine, $Mg(OH)_2$, Fe_2O_3 and H_2(g) but this process is relatively slow and not likely to be suitable for commercial application at the moment.

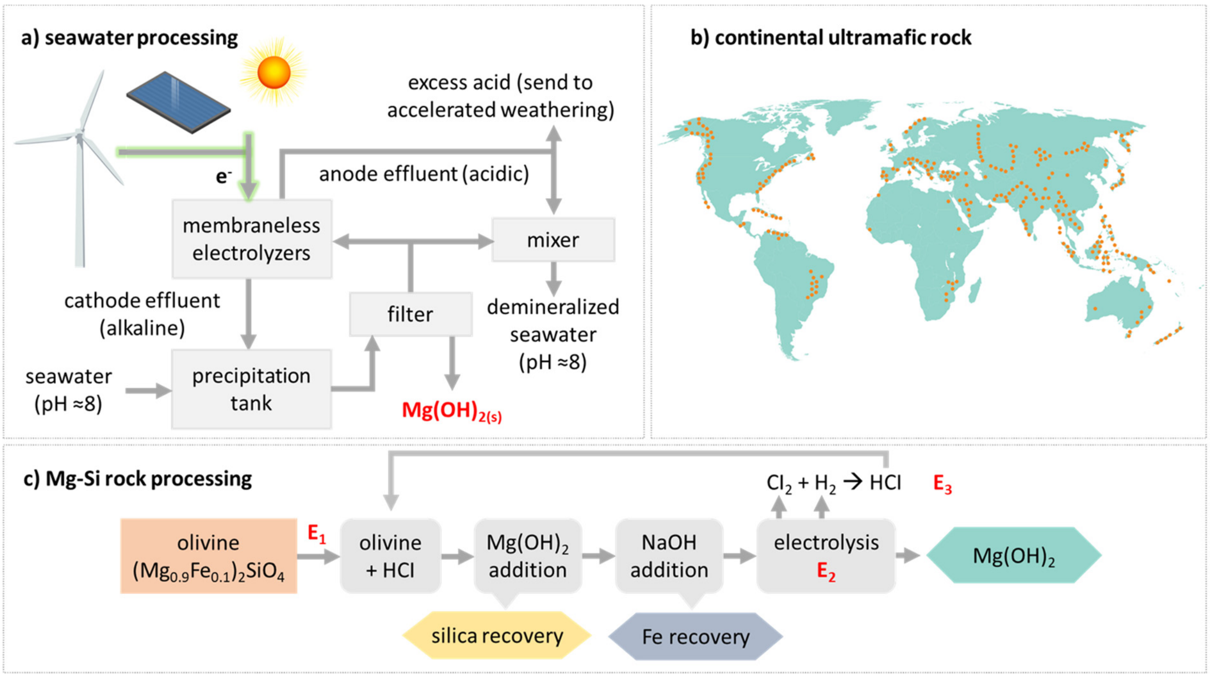

Figure 1. a) Currently known worldwide distribution of ultramafic rock (adapted from [23]); b) Process routes for Mg extraction from seawater (adapted from [14]); c) Process (acid) route for Mg extraction from silicates (adapted from [23]).

In the acid leaching approach (e.g. as shown in Figure 1c), finely milled olivine is combined with a strong acid, though weak acids can also be used, typically at temperatures less than 90°C. The Mg^{2+} in the olivine crystal structure is replaced by the H^+, resulting in the initial formation of $Si(OH)_4$ [26], as shown in Equation 1 for forsterite and hydrochloric acid. If Fe^{2+} is present in the olivine then an iron salt will be formed in addition to the magnesium salt.

$$Mg_2SiO_4 + 4HCl \longrightarrow 2MgCl_2 + Si(OH)_4 \tag{1}$$

There are two possible methods of production following initial digestions and separation of the silica and iron: pyrohydrolysis of the $MgCl_2$ solution [27], and use of electrolysis to generate the hydroxyl ions necessary to precipitate the $Mg(OH)_2$ from the $MgCl_2$ solution [23]. The first method of pyrohydrolysis produces MgO and HCl at temperatures of approximately 600°C, but requires evaporation of significant amounts of water from the magnesium salt solution, which can be very energy intensive. The second approach is conceptually similar to the recovery of $Mg(OH)_2$ from Mg-rich brines or seawater, as noted in Section 2.2, but uses electrolysis to generate the alkali component rather than using lime to precipitate the $Mg(OH)_2$. The electrolysis process also regenerates the acid which is used in the following digestions. Similar to the $Mg(OH)_2$ produced from the brine, the resulting $Mg(OH)_2$ can be calcined to produce MgO for use in cementitious cement systems. The electrolysis process can be energy intensive, consuming approximately 9 GJ of energy per tonne of olivine processed, but depending on the energy source, little or no CO_2 is emitted in the overall process.

Specific well-developed processes for Mg extraction from magnesium silicates (especially from serpentinites) are so-called ÅA-routes [28]. They rely on a mix of ammonium sulfate and ammonium bisulfate to dissolve the mineral, and can effectively utilize waste heat from industrial processes. In addition, if coupled with CO_2 capturing from the flue gases of a lime kiln using serpentinites or Mg-silicate mine tailings, the process will generate $MgCO_3$ with only 0.9 GJ of electricity and 2.6 GJ of heat needed per ton of CO_2 capture [29].

In the alkaline dissolution method, ground olivine (forsterite) is reacted with a strong base such as NaOH to form $Mg(OH)_2$ and silica, as shown in Equation 2a and 2b [24]. Although the reactions are relatively slow at temperatures of approximately 130°C, higher temperatures of 250°C provide greater efficiencies [30].

$$Mg_2SiO_4 + 2NaOH + H_2O \longrightarrow 2Mg(OH)_2 + Na_2SiO_3 \tag{2a}$$

$$Na_2SiO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SiO_2 \tag{2b}$$

As with the acid leaching electrolysis method, the recovered $Mg(OH)_2$ must be further calcined to produce MgO. $Mg(OH)_2$ could also potentially be used directly as a raw material with reactive silicate or carbonate sources [31–34].

In summary, the use of magnesium silicate minerals offers a potentially low carbon method to produce globally significant quantities of MgO. It should be noted that in addition to MgO, the mineral recovery process also generates a highly reactive silica that can be used along with the MgO to form an effective cement [35].

One of the most significant issues with the utilization of magnesium silicate minerals is the relatively high energy demand for the various processes. However, compared to the energy demand for alternative carbon capture and storage approaches, the additional energy associated with the processing of magnesium silicate minerals may not be that different. Magnesium oxide produced from magnesium silicates is currently not available in industrial quantities, though there are several companies and organizations working to commercialize this potentially low carbon manufacturing method.

3 Recent improvements and research needs

Different chemistries of MgO-based cements including Mg-oxysulfate, oxychloride, carbonate, phosphate, and silicate as well as their admixtures are presented. Figure 2 highlights how the different MgO-based cements group in terms of pH in comparison to Portland cement and alkali activated materials, another example of an alternative low-CO_2 binder.

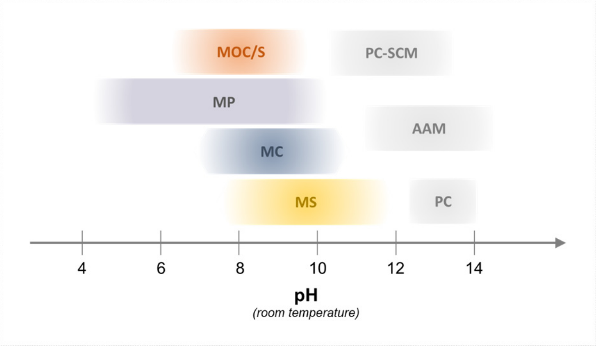

Figure 2. Approx. pH range for the stability of different MgO-based cement systems. MOC/S = Mg-oxysulfate / Mg-oxychloride cements, MC = Mg-carbonate cements, MP = Mg-phosphate cements, MS = Magnesium silicate cements, PC-SCM = blended Portland cements, AAM = Alkali activated materials, PC = Portland cement.

3.1 Mg-oxysulfate / Mg-oxychloride cements

Magnesium oxychloride (MOC) and oxysulfate (MOS) cements – including those which have long been known as “Sorel cements” - are receiving significant interest at present as potentially low-carbon, high-performing cements in niche applications [36, 37]. The chemistry and materials science of these cements has been discussed in detail in recent reviews [38, 39]. Ref. [38], in particular, focuses on the complexity of the crystallographic phase formation and stability relationships in these cements. Significant and ongoing research efforts are dedicated to understanding and characterizing the relationships between both stable and metastable hydrous oxysalt phases [40–43]. Another key research direction is in improving the water resistance of various types of oxysalt-based cements through the use of additives and modifiers [44]. Difficulties in achieving high water resistance are generally related to the significant aqueous solubility of the key binding phases (e.g. the so-called 5-1-8 and 3-1-8 phases in MOC cements, and the 3-1-8 and 5-1-2 phases in MOS cements, where the values written as *a-b-c* are the stoichiometric coefficients in the hydrate phase formulae $a\mathrm{Mg(OH)_2}\cdot b\mathrm{Mg(Cl_2,SO_4)}\cdot c\mathrm{H_2O}$) [43]. Modification of MOS by addition of a blend of citric acid and boric acid has recently shown the ability to stabilize some MOS phases for better mechanical and durability performance [45], and various waste-derived gypsums [46] and small biomolecules [47, 48] have been used to improve the water resistance of MOC in cementitious products.

Research on these materials has been particularly popular in regions which have ample magnesium brine resources, for example brine lakes or desalination by-products [49], as the availability of the necessary large quantities of $MgCl_2$ and MgO places limits on their larger-scale utilization elsewhere. Nonetheless, the high final strength and high resistance to chemical degradation in chloride-rich environments that can be achieved using MOC cements have led to their application in various roles including flooring [50] and wallboards [51], as well as for ornamental purposes [38]. While these cements are generally not compatible with conventional steel reinforcement – particularly MOC due to high chloride content – they are suitable for use with lightweight bio-based fillers including waste wood [52], sawdust [53], or rice husks [54], and also as concretes with conventional dense or lightweight aggregates [55].

3.2 Mg-phosphate (MP) cements

Magnesium phosphate (MP) cements show fast setting and high early strength and are thus used as rapid repair material, refractories and for special applications such as e.g. waste stabilization [56, 57]. MP cements are prepared using a soluble acid phosphate (commonly $NH_4H_2PO_4$ or KH_2PO_4; NaH_2PO_4 is less common due to its lower solubility) and harden in the presence of water through the reaction of phosphate with magnesia (MgO) resulting in the formation of struvite: $NH_4MgPO_4\cdot 6H_2O$, $KMgPO_4\cdot 6H_2O$ or $NaMgPO_4\cdot 6H_2O$ [58, 59]. Several other hydrates such as newberyite, bobierrite or cattiite are formed as intermediate phases during hydration. In commercial cement a surplus of MgO is used (which reacts only partially) to allow the early formation of stable 1:1 and 2:1 magnesium phosphates. The reaction between MgO and phosphates occurs fast, setting is observed within minutes, and different retarders such as borax, Al-salts or intermixing with fly ash, wollastonite or silica fume are used to slow down the reaction. Magnesium phosphates are also of interest for magnesium silicate cements, where phosphates are used in low dosages as dispersant [60–62].

3.3 Mg-carbonate (MC) cements

MC cements exhibit high potential as they can theoretically reach carbon-negative status, if certain conditions are provided. The hydration of MgO into $Mg(OH)_2$ and its carbonation under ambient conditions leads to the formation of various metastable hydrated magnesium carbonate phases (HMCs) with the general formula $x\mathrm{MgCO_3}$- $y\mathrm{Mg(OH)_2}$- $z\mathrm{H_2O}$ presenting cohesive properties. Alternatively, the formation of stable anhydrous $MgCO_3$ requires much higher pressures and temperatures [5]. Cement based on the carbonation of MOMS [2] showed a promising pathway to attain a very low-CO_2 and potentially even CO_2-negative concrete technology.

A detailed list of the compounds in the $MgO-CO_2-H_2O$ system is given in Table 1 where the phases are grouped according to their similarities in the number of Mg^{2+}, CO_3^{2-}, OH^- and H_2O. One of the main initiatives known in this area is Novacem's cement [63] involving a blend of MgO and HMCs. This combination resulted in a hardened cement, which contained brucite of low crystallinity after hydration [64, 65]. Another route to utilize these carbonates involves the production of plaster-like products [66, 67]. Glasser et al. [67] proposed two approaches to utilize nesquehonite ($MgCO_3 \cdot 3H_2O$) to produce plaster-like products: 1) thermal activation of the nesquehonite, followed by the rehydration of the precursor; or 2) direct curing of a slurry of nesquehonite at elevated temperature. The former was shown to be a promising pathway, where the product reached comparable compressive strengths as those of gypsum plasters [66].

MC-based cements have certain limitations, which are of interest to the research community. First, despite being the most stable form of magnesium carbonate, the formation of anhydrous $MgCO_3$ remains challenging due to 1) its high energy barrier, 2) large hydration energy of H_2O [5] and 3) lattice constraints on the spatial configuration of CO_3 groups in magnesite crystals [68] (see also the current review [69]). Second, since all HMCs are metastable in the $MgO-CO_2-H_2O$ system [70], the stability and transformation of these phases poses a risk to the long-term durability and consequently limit the use of these cements. Third, the low reaction degree of MgO due to the formation of passivation layers of $Mg(OH)_2$ and HMCs present an inefficient use of this cement from the CCS point-of-view. Finally, the need for ex-situ carbonation for rapid strength development can necessitate the need for specialized curing environments to enable the use of these cements in pre-cast applications.

In line with these limitations, recent improvements have shown some promising progress to overcome the above-mentioned bottlenecks and deliver better performance and efficacy in producing these cements. Blends of MgO and HMCs are being further investigated with the goal of developing ready-mix concrete mixes involving MCs as the main cement [64]. The reaction kinetics and degree of reaction of MgO and associated formation of HMCs have been enhanced via the inclusion of organic additives [71], MC seeds [72] and bacteria [73]. Additionally, the structure brucite formed in such carbonated materials contain water and carbonates [74, 75]. These improvements have enabled a more effective use of MCs and carbon in both ready-mix and pre-cast elements. In addition to the research initiatives on the enhancement of the properties of these cements, plaster-like materials and blended formulations involving the use of reactive MCs are also being developed. However, more efforts are still needed to 1) better understand the phase composition of MgO-HMCs blends, 2) lower the amount of unreacted MgO and/or $Mg(OH)_2$ under carbon curing, and 3) obtain data for long-term durability and performance of these cements.

3.4 Magnesium silicate (MS) cements

MS cements harden due to the formation of magnesium silicate hydrate (M-S-H) phases from the hydration of reactive sources of magnesia and silicate [38, 76]. MS cement produced by calcination and pulverization of magnesium silicate rocks and lime were patented at the end of the 19th century [77]. Further U.S. patents indicated that magnesia chloride cements were improved by the addition of silicates [78, 79]. In general, poorly crystalline M-S-H forms from the reaction between silicate and magnesia, $Mg(OH)_2$, $MgSO_4$ or $MgCl_2$ in a basic environment [76, 80].

Table 1. Compounds in the $MgO-CO_2-H_2O$ system.

	Chemical formula	Name
	MgO	magnesium oxide / periclase
	$Mg(OH)_2$	brucite
Group I	$MgCO_3$	magnesite
	$MgCO_3 \cdot H_2O$	monohydromagnesite
	$MgCO_3 \cdot 2H_2O$	barringtonite
	$MgCO_3 \cdot 3H_2O$	nesquehonite
	$MgCO_3 \cdot 5H_2O$	lansfordite
	$MgCO_3 \cdot 6H_2O$	hexahydromagnesite
Group II	$Mg_2(CO_3)(OH)_2 \cdot 0.5H_2O$	pokrovskite
	$Mg_2(CO_3)(OH)_2 \cdot 3H_2O$	artinite
Group III	$Mg_5(CO_3)_4(OH)_2$	magnesium carbonate hydroxide
	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	hydromagnesite
	$Mg_5(CO_3)_4(OH)_2 \cdot 5\text{-}8H_2O$	dypingite
	$Mg_5(CO_3)_4(OH)_2 \cdot 5\text{-}6H_2O$	giorgiosite
	$Mg_5(CO_3)_{4.7}(OH)_{0.3} \cdot 12H_2O$	protohydromagnesite
Group IV	$Mg_7(CO_3)_5(OH)_4 \cdot 24H_2O$	shelkovite

$$x\,Ca(OH)_2 + y\,Mg^{2+} + SiO_{2\,(am.)} + z\,H_2O \rightarrow M_y - S - H_z + x\,Ca^{2+} \tag{3a}$$

$$5Mg_2SiO_4 + 2SiO_2 + (7+z)H_2O \rightarrow 3Mg_3Si_2O_5(OH)_5 + Mg(OH)_2 + SiO_2 + z\,H_2O \rightarrow M - S - H_z \tag{3b}$$

M-S-H formation is also observed in geological environment in the presence of high pH values (>9) in the contact zone between Portland cement and Mg-containing solution [81]: M-S-H has been observed in cements in contact with river [82], clayey [83] or saline waters [84, 85] (Equation 3a) also forming during the serpentinization of olivine [86, 87] (Equation 3b).

In the last decades, MS cements gained interest in the context of nuclear waste management due to the lower pH of the matrices compared to hydrated Portland cements [88]. Additionally, MS cements show beneficial properties for radionuclide retention [89, 90] as well as for the immobilization of metallic wastes [31, 91]. Therefore, several recent studies have focused on the understanding of the structure and the stability of M-S-H phases [88, 92]. M-S-H phases are nano-crystallite hydrated phyllosilicates with relatively short coherence length, small particle size and thus large surface area > 200 m^2/g [92–96]. The alkalis and calcium can be sorbed in the interlayer or at the surface [97, 98]. Interestingly, once formed, M-S-H is stable over a large range of pH (7.5 to 12.5) [97, 99].

The formation of M-S-H is rather slow in the pure MgO-silicate water – mostly in laboratory experiments – due to a kinetic hindrance of brucite dissolution [100]. The presence of hexametaphosphate or carbonates can accelerate the reaction due to the formation of aqueous Mg complexes, leading to the destabilization of brucite [101–104]. The use of hexametaphosphate also strongly improves the workability, which leads to a lower water demand and thus lower porosity [101], such that M-S-H cements mixed with hexametaphosphate show 28-day compressive strength comparable to that of PC [101, 105]. More generally, the compressive strengths of MS cements depend strongly on the water content and thus, the porosity of the matrix [106]. However, we have a limited understanding of the properties of M-S-H itself or the microstructure of such cements. The physical properties of such cements or concretes from setting/hardening to drying or durability studies are not reported in literature.

To produce MS cements, both sources of MgO and SiO_2 are needed. If MgO is recovered from magnesium silicate rock as forsterite or serpentine [23, 28], the silica from the Mg-silicate separation could be used. However, this side product contains some iron, calcium, aluminum and alkalis depending on the separation process. Reactive clays produced by thermal or mechanical activation of globally available clay minerals could act as silicate sources as well. Such activated clays will contain large amounts of aluminates, but also iron compounds, alkalis and traces of calcium. The incorporation of aluminate in the main layer of M-S-H has been observed in M-S-H synthesized in the laboratory [107–109]. The presence of aluminates from reactive clays can lead to the formation of additional Mg-Al layered double hydroxide (Mg-Al LDH) together with M-(A-)S-H [110, 111]. The formation of Mg-Al LDH lowers the porosity and improves the mechanical properties [112–115]. Potentially Fe^{2+}/Fe^{3+} could also contribute to LDH formation [116] or be incorporated in M-S-H or Mg-Al LDH [117], although this has not yet been reported for M-S-H based cements.

3.5 Admixtures

Much less work on admixtures that could be used in MgO-based cements compared to PC systems has been reported. Mainly, three issues have been tackled so far: (i) reduction of the generally high water demand by the use of dispersing agents, (ii) adjustment of setting time with accelerators or retarders, and (iii) increase of the hydration degree of MgO with an emphasis on the enhancement of CO_2-sequestration due to enforced carbonation.

The high water demand of MgO-based cements needs to be reduced in order to provide sufficient mechanical properties. Dead-burnt MgO has been used as model material to study the adsorption of organic polyelectrolytes such as the polymers used in superplasticizers for PC-based concrete, as its surface chemistry and adsorption properties are comparable to those of PC [118, 119]. Thus, dispersing agents that work in PC-based cements, i.e. superplasticizers based on polycarboxylate-ether or naphthalene sulfonate, seem to work with MgO-based cements as well. However generally quite high dosages are needed for these cements e.g., MOC cement [120], MOS cement [121], MgO-based suspensions and paste [122–124], and MC cement [65]. Despite the high dosages, the retarding effect seems to be less than in the case of PC-based systems, and the addition of a retarder may still be necessary i.e. in case of MC cement (MgO-HMC blends) [65]. However, the types of superplasticizers developed for PC might not be perfect for MgO-based cements. This refers especially to MS cements, as silica fume shows incompatibility issues with certain superplasticizers [125]. Phosphate-based dispersants such as sodium hexametaphosphate (NaHMP) have been studied especially for magnesium silicate cements [101, 102, 126–129]. Besides significantly improving workability, they increase pH, thus increasing SiO_2 solubility. This alone would be problematic since the solubility of Mg is poor at high pH, however HMP suppresses brucite precipitation, therefore improving Mg solubility and increasing pH simultaneously [126]. Other additives such as CaO [130], sodium metasilicate [131], alkali carbonates [18, 132, 133] and NaCl [133] have also been used to enhance early and late age hydration kinetics. Furthermore, boric and citric acid are used to improve the mechanical properties of MOC [45] and polymer latexes to improve water resistance of MOC [134].

So-called "hydration agents" are used to enhance the reaction degree of MgO in carbonation-hardening construction products, thus facilitating the sequestration of CO_2. Such additions comprise of $NaHCO_3$, NaCl, $MgCl_2$, HCl, as well as sources of organic ligands such as magnesium acetate [65, 132, 133, 135, 136]. The pH range of MgO-based cements currently makes them only suitable for unreinforced concretes, therefore eliminating concerns of Cl on steel rebar corrosion. These organic ligands proved to be very efficient in increasing the reaction degree of MgO, the amount of Mg ions in the liquid phase, the amount of sequestered CO_2 and the mechanical properties. Furthermore, the hydrate assemblage of the carbonated paste is altered, stabilizing a giorgiosite-like phase in favour of dypingite [136]. Nucleation seeding by the addition of HMCs is a further option to enhance reaction and carbonation kinetics in such systems [72, 137].

4 Potential of thermodynamic models to predict the composition of MgO-based cements

Over the last decades, thermodynamic modelling has been established as an efficient tool to predict the kind and amount of hydrates forming in hydrated PC, blended cements, calcium sulfoaluminate, calcium aluminate, alkali activated and magnesium phosphate cements [138, 139]. In hydrated Portland cements, blended and alkali activated cements the prediction of the "fate" of magnesium is hampered by incomplete and contradictory data for hydrotalcite-like phases (Mg-Al layered double hydroxide, Mg-Al LDH) [138, 140], which are the expected Mg-containing phases in such systems. Mg-Al LDH are difficult to observe by XRD due to their low crystallinities and their varying composition. Thus in the recent years, several groups experimentally investigated the solubility of Mg-Al LDH with varying compositions [141, 142], which led to additional, partially contradictory solubility data, while data for Fe-containing LDH are still largely missing.

For M-S-H, the nano-crystalline solid solution characteristic for hydrated magnesium silicate cement with a variable composition (Mg/Si ratios between 0.8 to 1.5 and H_2O/Si from 1.5 to 5), data related to solubility, heat capacity and entropy data have been determined in the last years [100, 143, 144]. The derived solubility data indicate that the poorly crystalline M-S-H is slightly more soluble than crystalline magnesium phyllosilicates such as talc or antigorite. Preliminary thermodynamic models to describe the uptake of aluminum in the main layers and of calcium or alkalis as exchangeable cations have been published [97, 98, 109], although formulation of a thermodynamic solid solution model taking into account the structural knowledge is still missing. Thermodynamic models for the uptake of other cations or anions are not available due to a lack of systematic experimental data. Finally, also data for MgO-based zeolites, which could form in the presence of aluminum, are not available.

For HMCs, well-determined thermodynamic data are available for nesquehonite, hydromagnesite and dypingite [145, 146], while data for artinite, monohydromagnesite, barringtonite, lansfordite and hexahydromagnesite are estimated [147] or indirectly calculated from calorimetric measurements [148]. Additionally, the stability of these carbonates is strongly influenced by temperature. Thermodynamic data are not known for the unknown poorly crystalline phase reported by Refs. [64, 65], or for phases such as pokrovskite, giorgiosite, hydrated dypingite, protohydromagnesite or shelkovite. As many different types of magnesium carbonate hydrates can potentially precipitate near ambient temperatures (Figure 3) depending on CO_2 pressure, pH values, relative humidity, time and temperature and as the conversion observed in such HMCs is slow, thermodynamic modeling is needed to gain a deeper understanding of the full system. At present, however, many missing or estimated data for HMCs and poor knowledge of the factors determining their precipitation kinetics, prevent reliable thermodynamic predictions for MC cements, as discussed in Refs. [65, 104].

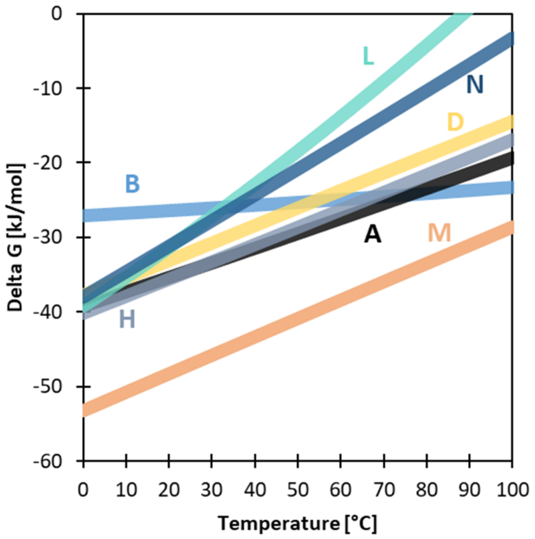

Figure 3. Free energies relative to MgO in kJ/mol as a function of temperature at pCO_2 =0.4 mbar and saturated vapour pressure for different HMC. A: artinite, D: dypingite. H: hydromagnesite, L: lansfordite, M: magnesite, N: nesquehonite. Calculated based on the thermodynamic data compiled in [104].

For MOC, MOS and MP cements, carefully derived thermodynamic datasets are available [149–154]. The main hydrate phases in MP cements, K-, Na- or NH_4-struvite, are relatively stable at above neutral pH values and ambient temperature, but are converted to phases with less water at slightly increased temperatures. At neutral pH different orthophosphates such as cattiite and bobierrite are stabilized and newberyite at pH 6 and below [150]. The phases formed in MOC and MOS systems, such as:

$Mg_2(OH)_3Cl{\cdot}4H_2O$,
$Mg_3(OH)_5Cl{\cdot}4H_2O$,
$3Mg(OH)_2.MgSO_4{\cdot}8H_2O$,
$5Mg(OH)_2{\cdot}MgSO_4{\cdot}2H_2O$, or,
$Mg(OH)_2{\cdot}MgSO_4{\cdot}5H_2O$,

however, are highly soluble, i.e. in equilibrium with magnesium, chloride and/or sulfate concentration in the range of several mol/L, such that specialized ion activity corrections for highly saline solutions such as the specific ion interaction theory (SIT) or the Pitzer equation should be used together with the respective set of ion interaction parameters [155, 156].

Missing thermodynamic and structural data, in particular for hydrated magnesium carbonates but also for magnesium based zeolitic precursors, or only partially established thermodynamic data (LDH, uptake of ions in M-S-H, ...) limit the potential of thermodynamic modelling to predict the hydrate composition of magnesium-based cements. There is an urgent need to determine experimentally the missing thermodynamic data for a range of solids as well as of potential aqueous complexes. In addition, the different ion activity models used in high (SIT, Pitzer [155, 156]) and low (often extended Debye Hückel [138]) ionic strength systems need to be merged in a single ion activity model, a challenging task due to the lack of Pitzer parameters describing specific ion interactions of Al-Mg, Mg-Si and Al-K, and the limitations of the extended Debye Hückel [138] to ionic strength of < 1 M.

5 Atomistic modeling of MgO-based cements

Atomistic modeling of cement-related systems has gained considerable interest in the last decade, yet MgO-based cements have not been between the most active areas of research, and few studies can be found in this context [157, 158]. Nevertheless, there are some aspects of MgO-based cements that might help in a fast implementation of atomistic modeling. First, both reactive and binding phases are predominantly crystalline, in contrast to the C-S-H gel in PC [159], which reduces the uncertainties about atomic models and simplifies the simulations. Second, the geochemistry community has worked intensively on the simulations of MgO-based minerals for the last 20 years. Their main interest has been the weathering and carbonation of Mg-silicates [160, 161] and the formation of Mg-carbonates, usually in comparison/combination with their Ca counterpart [147, 162, 163]. Thus, the physicochemical processes of interest are virtually the same in geochemistry and cement chemistry (dissolution, complexation, nucleation and growth, etc) and there is a well-established literature background on which to stand. Finally, and linked to the previous, computational tools, and particularly force fields for molecular dynamics simulations, have been already developed. The most common force fields used in cement research have their counterpart for MgO-based systems: core-shell potentials [164], ClayFF [165] and recently ReaxFF [166, 167]. These potentials should be tested carefully before extensive use, and reparameterization for specific problems might be necessary in some cases. Overall, there is a good pool of computational methods and literature knowledge that will serve as a starting point for future research in the field.

Regarding the potential use of atomistic simulations, we must take into account that the time and size limitations, hundreds of ns and tens of nm, makes it impossible to study directly macroscopic processes. To uncover their full potential the simulations should be carefully designed to target aspects complementary to the experiments. For instance, atomistic simulations could be used to provide thermodynamic data of MgO-phases to complete or refine thermodynamic databases [168]. Another potential field is the speciation and complexation of Mg ions in solution [169], which is critical in dissolution and nucleation, and for the design of admixtures. It is interesting to notice that, despite the structural and chemical similarity between certain CaO- and MgO-based phases (brucite/portlandite, sanderite/gypsum, magnesite/calcite, fosterite/γ-dicalcium silicate), Ca and Mg solubility and kinetics are considerably different. The variation can be attributed to the stronger Mg-O bonding, which translates into less reactive solids [170] and stronger Mg-water solvation shells [171]. Atomistic simulation could help in understanding reaction mechanisms, quantification of activation energy barriers, and guide the design of solubility agents and admixtures, always in combination with experimental work.

6 Opportunities and limitations for the different cements

In regions, where sustainable MgO derived from Mg-silicate rocks and/or Mg-rich brines will be plentiful, there will be some interest in the development and use of MgO-based cements for general usage in non-reinforced concretes, other non-structural applications or natural fiber reinforced composites. However, if a significant impact in terms of CO_2-savings is targeted, the use of MgO-based cements in structural applications is mandatory. This means solutions for improving the suitability of steel rebar or alternative reinforcement in MgO-based concretes should be actively sought. In this section, we discuss the opportunities and current bottlenecks for MgO-based cements.

6.1 MOC/MOS cements

The MOC/MOS are already commercialized and are the most advanced systems compared to the MC and MS cements. Their attractive surface finish and high strength (leading to high abrasion resistance) bring some interest in their use for industrial flooring. The high bound water content of several of the important MOC and MOS hydrates, and the low thermal conductivity that can be achieved (particularly with the use of lightweight and/or bio-based aggregates), lead to interest in the use of these materials in fireproofing applications and internal wallboards. However, broader usage will probably always remain to some degree restricted by the combination of geographic constraints on the raw materials supply, and the difficulty associated with achieving a stable hydrate phase assemblage that is resistant to environmental moisture. Magnesium oxysalt phase diagrams are rich in phases that are stable and/or metastable under different concentration/humidity/temperature conditions, meaning that the properties of the resulting cements tend also to be rather sensitive to formulation and application conditions.

6.2 MP cements

MP cements possess the highest mechanical performance of the so-far known MgO-based cements, and is currently in use in niche applications, such as industrial flooring or rapid repairs. Nevertheless, phosphorus is a critical fertilizer that cannot be recycled with the known technologies, and its resources are dwindling. Phosphate rock is a non-substitutable, non-renewable natural resource, which is essential for global food security. Affordable access to phosphorus is imperative to ensure global food provision and insufficient phosphorus fertilizer use in many parts of Africa will likely lead to crop yield reductions of nearly 30% by 2050 [172, 173]. There are no sustainable feedstocks for MP cements, that would not impinge on global food production such that MP cements should not be used as a mass product in construction industry. However, phosphates – although in low quantities - are also present in dispersants such as sodium hexametaphosphate (NaHMP), which are particularly effective for magnesium silicate cements and its use as a minor additive contributes significantly to lowering the water demand. Focused research is needed to assess the environmental footprint of phosphate as minor additive in other MgO-based cements.

6.3 MC cements

MC cement has the potential to be a carbon-negative cement as they can uptake CO_2. With the current advances in MgO extraction (i.e., from Mg-silicates or the Mg-rich brines), the cost and energy required to produce MgO can be brought down to the level that carbon capture and utilization can create revenue and profits. Additionally, if magnesium carbonates can form in its most durable form (anhydrous magnesium carbonate or possibly also hydromagnesite, which occurs in natural deposits), the final product can store carbon for millennia and can be used as fillers such as aggregates in construction. A promising first application of this cement is to produce non-load-bearing structures such as bricks, or plasterboard products, which have less strict requirement for service-life performance. Furthermore, if MCs can be produced in reactive forms, this opens up opportunities for their use as supplementary cementitious materials (SCMs) in cement blends or for improving the performance of MgO-based cement.

The current limitations of MC cement are as follows: 1) Variability/availability of raw materials in different parts of the world 2) lack of long-term data for durability performance, 3) in-depth understanding of the phase transformation among different HMCs and the ability to model this phenomenon (e.g., via thermodynamic modelling), and 4) the lack of holistic assessment for techno-economic viability of mass producing this cement.

6.4 MS cements

If reactive silicate/aluminate are by-products of sustainably-sourced MgO, MS cements could become attractive. Compared to MC cements, they can generate higher compressive strengths without relying on carbonation [76]. The combination of the MC and MS chemistries seems promising to obtain a cement with both relatively low carbon footprint and optimized performance. However, the stability of M-S-H versus the stability of HMCs is not yet understood. MS cements could also be used as cements for building materials containing natural fibers or bio-aggregates [174, 175] as they present lower pH values and seem to be more compatible with such organic-based aggregates than PC systems [175–177]. Finally, the M-S-H phases are very stable [178] and present a strong potential as durable cements for low-CO_2 construction.

Excluding the availability of the raw materials, the main limitations are related to 1) the implementation, i.e. the fresh properties and early mechanical properties linked to the slow reaction rate, 2) the lack of fundamental understanding of the effect of the elements such as aluminum, iron, calcium on fresh and mechanical properties; and 3) the lack of long-term data on durability.

7 Conclusions

Magnesia-based cements come in multiple flavors, with each one possessing attractive features for different applications. Their current use remains limited by geographic constraints on the MgO supply and available MgO extraction technologies. Considering the various applications and high competition for these raw materials with other markets (i.e., magnesium is considered as a critical raw material by the European Union [179]), establishing a sustainable long-term supply for MgO or its derivatives with cementitious properties are essential.

Research is actively ongoing in multiple fronts, especially driven by the need for large scale carbon capture and utilization/storage applications, as well as the need for low-CO_2 cements and SCMs. Current limitations that should be addressed by research include the lack of thermodynamic data for many of the phases of interest, as well as the lack of long-term studies on durability and microstructural changes. Furthermore, admixtures tailored for magnesia-based systems have not been investigated, which could play a critical role in facilitating the use of MgO cements in large scale applications. While non-structural applications are initially attempted, the use of these binders in structural concrete is needed to make a significant impact in the reduction of CO_2 emissions. To enable their use in structural applications, the compatibility of these binders with traditional as well as other types of reinforcement needs to be investigated. Due to the low pH of MgO-based concretes, mild steel reinforcement might not be suitable without adjustments to the mix design and/or curing conditions. Furthermore, techno-economical assessments, as well as life cycle assessments are still largely missing or are implicit, which is natural given the low technology readiness level (TRL <5) for the different applications.

To conclude, magnesia-based cements are emerging technologies and an active area of research with increasing number of parties that are interested in these products. A new RILEM Technical Committee (MBC: Magnesia-based binders in concrete) [180] has recently been established on the topic, with the aim of improving understanding and coordination in the nascent field as well as to formulate a research roadmap to initiate the applications of MgO-based binders in the construction industry.

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Authorship statement (CRediT)

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