



Article MgO-Based Cementitious Composites for Sustainable and Energy Efficient Building Design

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Abstract: Concrete made with Portland cement is by far the most heavily used construction material in the world today. Its success stems from the fact that it is relatively inexpensive yet highly versatile and functional and is made from widely available raw materials. However, in many environments, concrete structures gradually deteriorate over time. Premature deterioration of concrete is a major problem worldwide. Moreover, cement production is energy-intensive and releases a lot of CO₂; this is compounded by its ever-increasing demand, particularly in developing countries. As such, there is an urgent need to develop more durable concretes to reduce their environmental impact and improve sustainability. To avoid such environmental problems, researchers are always searching for lightweight structural materials that show high performance during both processing and application. Among the various candidates, Magnesia (MgO) seems to be the most promising material to attain this target. This paper presents a comprehensive review of the characteristics and developments of MgO-based composites and their applications in cementitious materials and energy-efficient buildings. This paper starts with the characterization of MgO in terms of environmental production processes, calcination temperatures, reactivity, and micro-physical properties. Relationships between different MgO composites and energy-efficient building designs were established. Then, the influence of MgO incorporation on the properties of cementitious materials and indoor environmental quality was summarized. Finally, the future research directions on this were discussed.

Keywords: MgO-based cement; sustainability; energy efficiency; sustainable materials; green architecture

1. Introduction

The adage "all old is fresh again" surely applies to the existing condition of magnesiabased cements (MgO). The worldwide building materials sector, which has been traditionally focused on a wide variety of materials suitable for local requirements and individual uses, became almost a monoculture based on the use of Portland cement (PC) during the latter half of the twentieth century, with the other materials largely overlooked. Because of the fast growth of the building sector, the production of Portland cement and natural aggregates has risen at an unprecedented rate. In fact, the building industry required around 40 billion tons of aggregates and 4 billion tons of cement in 2014 [1,2]. As a result, mostly during the manufacturing of these products, a large volume of carbon dioxide (CO_2) is emitted into the atmosphere. For instance, to generate 1 ton of cement, 125 kW of energy is needed, as well as 0.89 tons of CO₂ emissions into the atmosphere [3,4]. Implementing renewable materials into concrete, such as fly ash (FA), silica fume, slag, metakaolin, and industrial byproducts, is one way to address this problem [5-10]. Incorporating MgO into concrete is another choice for making it more natural. Cements with a high MgO content have become increasingly common in recent years, owing to the concern about climate change and the need to reduce CO_2 emissions associated with the manufacture of traditional Portland cements. Some scholars assume that cements with a high MgO material can



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). be made with lower CO_2 emissions [11]. Other scholars assume that by trapping ambient CO_2 and converting it to magnesium crystals, it is possible to make cement with a positive CO_2 balance (carbonates and hydroxycarbonates). Carbonation of MgO is defined as the formation of magnesite from MgO as a result of the absorption of CO_2 [11].

In such pyrolysis and reaction situations, the use of MgO will reduce thermal shrinkage [12,13]. It is also possible to decrease the expense of concrete by eliminating the need for expensive curing steps and speed up the manufacturing process by continually casting concrete without the need for too many cold joints [14]. However, environmental concerns were the driving force behind the production and increasing capacity of MgO-based cements. Because of the need for MgO production by cooler altitudes (relative to the desired rate for processing $CaCO_3$ in ordinary Portland cement (OPC)), as well as the fuel savings related to low temperatures, many people see MgO-based cements as a key component of the future of environmentally sustainable cement manufacturing. Natural resources such as soil, stone, and timber are appropriate building materials for low carbon emissions and footprints and recycling or reuse potential. Natural materials that are unprocessed or minimally processed have limitations, notably in terms of strength and durability. Energy is expended in the processing and transportation of raw materials, resulting in carbon emissions. To reduce carbon emissions, developing technologies that allow building materials and products to be made with the least amount of energy [15]. The building industry is interested in the development of carbon-neutral cementation pathways as a significant challenge. Capturing CO₂ released during the calcination of limestone, and perhaps reusing it, is a very appealing technique to attain this goal. To that purpose, this research investigated the importance of reaction parameters, including time, temperature, and pressure, affect the rate of Ca(OH)₂ carbonation under both liquid and supercritical CO₂ exposure [16]. Similarly, MgO's capacity to absorb carbon dioxide from the air to shape a range of carbonate and hydroxycarbonate blends are on point with "carbon neutral" cements, which can absorb almost as much CO_2 over their lifespan as they emit during manufacturing. These two intertwined factors have sparked a recent surge in research and business involvement in MgO-based cements.

This paper starts with the characterization of MgO in terms of environmental production processes, calcination temperatures, reactivity, and micro-physical properties. Relationships between different MgO composites and engineered cementitious composites are then established. Next, the influence of MgO incorporation on the properties of cementitious materials and indoor environmental quality are summarized. Finally, future research directions are discussed.

2. Materials and Methods

2.1. Production of Magnesia and Its Use in Cementitious Materials

The construction industry is responsible for a multitude of environmental problems worldwide. It is an energy and resource-intensive industry that generates significant emissions and waste. While steel and concrete are the most commonly used construction materials, each has its own advantages and disadvantages based on price, properties, and structural capabilities. Recently, however, there has been increased concern about the environmental impact of their production and use. Cement, for example, is widely known to be a key ingredient in the production of concrete used in the construction of buildings and other physical infrastructures. The production of cement, in turn, consumes a significant amount of energy. Despite significant technological advances, the world continues to be plagued by health risks and other environmental disasters caused by cement manufacturing companies. Emissions from cement manufacturing harm the environment, degrade air quality, and have a major impact on climate change, contributing significantly to global warming [17].

For avoiding environmental problems, scientists are always searching for sustainable structural materials that show high performance during both processing and application. One way to overcome this issue is to partially replace Portland cement with industrial waste products, e.g., blast furnace slag, fly ash, micro-silica, natural pozzolans, and limestone fillers. Supplementary cementitious materials (SCMs) contribute to the qualities of hardened concrete by hydraulic and/or pozzolanic activity when used in conjunction with Portland cement, Portland limestone cement, or blended types of cement. Supplementary cementitious materials provide long-term and performance benefits to persons who construct and occupy various structures [18]. Several performance factors, including improved workability and consolidation, flexural and compressive strengths, pumpability, resistance to chlorides and sulfates, lower temperatures for mass concrete, mitigation of alkali-silica reaction, and decreased permeability, have contributed to the growing use of these environmentally friendly materials. The use of cementitious blends not only results in stronger, more lasting high-performance concretes but also helps minimize the global climate impact by cutting energy consumption and greenhouse gas emissions. These materials provide a substantial contribution to environmentally friendly buildings. The use of these materials in concrete manufacturing consumes less energy and delivers increased efficiency and building performance [19,20]. These SCMs are not only effective in lowering the environmental impact but also have the potential to enhance the durability of concrete. Some SCMs can modify microstructure by forming additional hydration products. This refines the pore structure and decreases the penetrability of concrete. Magnesia (MgO)-based cementitious composites are another foremost approach towards sustainable design and for promising to attain targets. It is possible to produce environmentally friendly cement with a high MgO content associated with reduced CO₂ emissions.

Cement filler substitutions alter microstructural development in a variety of ways. The particle effect (on hydrate nucleation and dilution of the reactant in a larger volume of water) is distinguished from the hydration of the fillers in the cementitious matrix. As already stated, siliceous SCMs provide silica (reacting with calcium aluminate hydrates to form a new stable) phase-filling space during the hydration and curing. In the second part of the dissertation, we aim to better understand the formation of cement paste and mortar, such as stratlingite, and their influence on the space-filling properties of mortars [21].

Magnesium, at 2.3 percent by weight, is the eighth most common metal in the Earth's crust and is found in a variety of volcanic rocks like olivine, magnesite, and iron oxide. Magnesium is, indeed, the third most common compound in ocean water, with amounts of around 1300 parts per million. The MgO demand is currently 14 million tons per year (USGS, 2012), in comparison to over 2.6 billion tons for OPC, with current prices of about GBP 200 per ton for responsive MgO (calcined), relative to BGP 70 per ton for OPC. The fresh method is used in most industries to produce cement, and it comprises of the following steps: refining and heterogenization of raw materials (to collect raw flour); clink erization of the fresh flour in domestic fuels (to produce clinker); resulting in clinker cooling; refining of clinker and application of gypsum to produce cement; packing and shipment of the end product. This method consumes a lot of energy and produces a lot of air pollution because it needs temperatures as high as 1400 degrees Celsius. Magnesia (magnesium oxide, MgO) is made mostly by calcining magnesite, which is usually the method of making lime from limestone. Seawater and brine streams, as well as other sources, provide a smaller proportion of the world's MgO [22].

Since concrete's roles in the community are pretty scarce in life, and its hydration compound brucite [Mg (OH)₂] appears in only a few commercially feasible geological formations, commercially extracted magnesium oxide (commonly referred to as magnesia or periclase) is not mined specifically. Alternatively, MgO is typically obtained via a dried route from calcination of extracted magnesite mines (MgCO₃) or a moist route from magnesium-bearing drilling fluids or ocean water substances. As well as the high energy processing needs via the wet path, calcination of magnesite accounts for the majority of MgO global production [22]. The dried path for MgO processing usually necessitates magnesite crushing prior to calcination via the process, and MgO-alkaline oxide plays an electron donator role in water, as shown in the equations below:

$$MgO_{(s)} + H_2O \rightarrow Mg(OH)^+_{(surface)} + OH^-_{aq}$$
(1)

OH[–] anions are adsorbed on the positively charged surface:

$$Mg(OH)^+_{(surface)} + OH^-_{aq} \rightarrow Mg(OH)^+ \cdot OH^-_{surface}$$
 (2)

 OH^{-} anions desorbed from the surface, releasing Mg^{2+} and OH^{-} ions into the solution:

$$Mg(OH)^+ \cdot OH^-_{surface} \rightarrow Mg^{2+} + 2 OH^-_{aq}$$
 (3)

Ion concentration reaches the solution supersaturation (pH~10.5), at which point the hydroxide starts to precipitate as brucite on the oxide surface:

$$Mg^{2+}_{(aq)} + 2 OH^{-}_{(aq)} \rightarrow Mg(OH)_{(2(s))}$$
 (4)

Here, it should essentially be aimed at increasing the quantity of CO₂ and increase the formation of HHMs, and the general mechanical performance of the formulations obtained by increasing MgO hydration.

Since Fe₂O₃ and SiO₂ contaminants may adversely impact MgO's refractory use, higher-grade MgO necessitates the careful selection of MgCO₃-bearing rocks or thermal treatment [22]. The wet path is more complicated chemically, but it usually involves precipitating Mg(OH)₂ from a magnesium-rich solution as a way to solve seawater or (more dilute) saltwater. Water is pumped into an MgCl₂-rich precipitation and transferred to the groundwater to add pressure in Veendam, the Netherlands. Groundwater has an average magnesium concentration of 1.29–1.35 g/L, which varies by area. As a result, groundwater is a huge source of magnesium. Ion-exchange adhesives can also be used to deborate condensed brines or coastal areas, and sulfate concentrations can be decreased by adding CaCl₂ brines to instigate CaSO₄•2H₂O and yield filtered MgCl₂-rich saltwater [22].

2.2. Development of Reactive Magnesia Cements

Increased populations directly reflect improvements in health and mortality rates over time, leading to further population expansion. Rising populations, on the other hand, indicate an increase in pressure on existing social facilities, such as housing. As the demand for housing increases exponentially, the construction sector and production of traditional materials such as cement, steel, aluminum, and wood, will be even more strained. According to studies, the production of traditional building materials, such as cement, consumes a significant amount of thermal and electrical energy resulting in higher construction costs [23].

However, as some have noted, the housing supply is inadequate for a variety of reasons. First, poor urban planning limits urban expansion due to a lack of land and infrastructure. Second, insecure land tenure and high urban land costs are exacerbated by various land tenure regimes and ineffective land administration and governance institutions. Third, since housing finance markets in Africa are underdeveloped, most Africans have to rely on self-financing and incremental construction methods to obtain houses. Most importantly, the high cost of construction puts houses out of reach for the majority of low-and middle-income families [17].

Moreover, such manufacturing processes have a larger carbon footprint and pollute the air, land, and water. For example, studies show that the calcination process used to make cement requires temperatures up to 1450 °C and emits about 0.85 tons of CO_2 per ton of cement produced. According to another study, buildings in France account for about 23.5 percent of greenhouse gas pollution due to the use of traditional building materials. In a similar vein, others have claimed that the construction industry is currently unsustainable. These findings suggest that further scientific research is needed to develop building materials that are not only more environmentally friendly and sustainable but also more economical without compromising construction quality [23].

The calcination process of reactive MgO requires a lower temperature (700–1000 $^{\circ}$ C for reactive MgO vs. 1450 $^{\circ}$ C for PC), which allows the use of alternative fuels with low

calorific values (e.g., refuse-derived fuel and hybrid). By interacting with H_2O and CO_2 to bind CO_2 and build strength, the reactive MgO creates the binding property. Figure 1 shows the variables that affect the hydration of MgO.



Figure 1. Factors influencing the hydration process. Reprinted with permission from Ref. [14]. Copyright 2014 Elsevier.

There has already been a revival of excitement in dynamic magnesia (MgO) cements with a high MgO component in recent decades, but most of the research was already published in the field of quality management or web outlets rather than peer-reviewed journals [24]. Whenever the responsive MgO is generated in a carbon-recycling cement kiln, the subsequent CO_2 absorption (by the cement in operation) is taken into account. Based on a 2001 application, Harrison of the Australian company TecEco was granted a patent in the United States that explains the use of expanded curing periods and occasionally steamcuring to manufacture solid blocks made of MgO, pozzolan, and PC [25,26]. The MgO used is made by calcining MgCO₃ at a low temperature of 800 $^{\circ}$ C; this causes layer strain and permeability in MgO samples that would otherwise be coated at higher temperatures. This allows for the precise regulation of MgO reactivity based on treatment conditions and particle shape, ensuring that it hydrates at the same period as the other cementitious materials [25]. Pertinently, this MgO responds much faster than kilned MgO (low-reactivity MgO calcined at >1500 $^{\circ}$ C), including the free MgO in Portland (clinker), which has been fired, often at extreme temps, and thus normally hydrate slowly, causing cracking within traditional cements as an expansive reaction rate is caused centrally within a hardened substrate [26]. MgO has little impact on the formation of PC hydrate processes after up to four weeks of hydration [27–29]. Many tests have shown that some responsive MgO– PC-blended cements do not absorb a detectable amount of CO_2 from the atmosphere within the period of curing and are hence impossible to be carbon-negative, or even carbonneutral, in the appropriately limited period. Once MgO is applied to a PC-based device, Cwirzen and Habermehl-Cwirzen [25] found that now the freeze-thaw tolerance, flexural and compressive strengths are decreased due to higher capillary permeability. Figure 2 shows low magnification scanning electron micrographs of fractured surfaces of all types of samples at 14 days.

Nevertheless, when accelerated-carbonation healing criteria were applied to responsive MgO structures, a very opposite result was obtained. Until being split onto 5-mm-thick specimens, MgO/PC/FA- and MgO/FA-based cements became air preserved for two weeks at 98% moisture content (MC). Such specimens were again preserved for another

two weeks, whether in the air at 98% MC as a monitor or in monitored CO₂ atmospheres at atmospheric pressures including 5 or 20% CO₂ by volume, at 65% or 95% MC [29].



Figure 2. Low magnification secondary electron micrographs after 14 days of curing of the 50% and 90% pfa content mixes: (**a**) MgO_{0.1}-pfa_{0.9}, (**b**) (MgO_{0.8}PC_{0.2})_{0.1}-pfa_{0.9}, (**c**) (MgO_{0.5}PC_{0.5})_{0.1}-pfa_{0.9}, (**d**) PC_{0.1}-pfa_{0.9} Factors influencing the hydration process. Reprinted with permission from Ref. [24]. Copyright 2008 Elsevier.

Mo and Panesar recently published research on responsive MgO, focusing on the rapid carbonation of MgO/PC blends both with and without the inclusion of surface granulated blast-furnace slag (BFS) [30]. Such cements produced up to 40% MgO, with MgCO₃•3H₂O and CaCO₃ even as the main carbonate compounds produced (both calcite and aragonite polymorphs). Cement materials were vacuum-dried to extract the capillary humidity before even being subjected to a 99.9% CO₂, 98% MC, allowing for accelerated carbonation of the collections. The existence of MgO was said to change calcite composition, leading to the formation of magnesian calcite that, in combination with the accumulation of MgCO₃•3H₂O, decreased sample porous structure, densified the microstructure, and increased microhardness [31]. Due to the comparatively harsh carbonation circumstances, it is unclear if this carbonation system will be used commercially or on a broader scale.

2.3. Expansive MgO Cements

It's worth noting that responsive MgO cements are different from limited proportion reactive MgO as a comprehensive additive in cement binders, which are commonly used in dam building and other major construction projects, especially in China. This is to substitute for PC's natural hydration shrinkage, which can last weeks or months in operation [32]. The usage of decent low cements or the intensive need for supplemental cementitious materials will help only with the cooling shrinkage of cement paste during toughening, which can be mitigated by using massive cement/concrete edifices. This really is attributable to the fact that cement hydration is strongly exothermic, releasing upwards of 500 J/g of cement. When the temperature goes up in reach of 50 °C, after the concrete has been cured (up to six months after casting), hydration of the cement in such massive amounts of concrete occurs [9,33].

In 1867, Sorel cement or magnesium oxychloride cement (MOC) was discovered. MOC was prepared by mixing magnesium oxide (MgO) with magnesium chloride (MgCl₂) [33]. The MgO/MgCl₂ and H₂O/MgCl₂ molar ratios are the main parameters, which potentially affect the mechanical properties of MOC [34]. The main hydration products of MOC, which are responsible for its hardening and strength, are 5Mg(OH)₂•MgCl₂•8H₂O (phase 5),

 $3Mg(OH)_2 \bullet MgCl_2 \bullet 8H_2O$ (phase 3) and $2 Mg(OH)_2 \bullet MgCl_2 \bullet 8H_2O$ (phase 2). The composition of hydrate phases mainly depends on the MgO/MgCl₂ molar ratio [35]. The mechanism of hydrate phase formation includes three steps: the first is the neutralizing process in which MgO powder is neutralized by free H⁺ produced from the dissociation of MgCl₂ crystals in water. The second includes the formation of bi-nuclear, tri-nuclear, and poly-nuclear complexes $\{Mg_x(OH)_y(H_2O)_z\}^{2x-y}$ by the hydrolyzing-bridging reaction. In the final step, the condensation of these phases and the adsorption of Cl⁻ (to equalize the positive charge on complexes) have occurred, leading to the formation of an amorphous gel, which crystallized in a few days or weeks [35]. MOC characterizes by low thermal conductivity, high early strength, high firing, and good abrasion resistivity [36]. Although advantageous properties, the MOC showed poor water resistivity, limiting its application for practical engineering projects.

Based on the mechanism of MOC formation [35], MgO cement has been considered a good alternative to traditional Portland cement. MgO-based composites have been characterized by their high strength, early hardening, and strong adhesion strength. However, the inherent brittleness of these composites may restrict the number of application areas in practice. To overcome this issue and extend the application range of these composites within the construction industry, MOC-based engineered cementitious composites (MOC-ECC) have been developed.

When the concrete cools down, it expands, resulting in a crack-prone dam. Various structural engineering ventures have long used shrinkage-compensating and expansive cements [36–39]. These really are traditionally dependent on applying ye'elimite $(Ca_4Al_6O_{12}SO_4)$ with anhydrite $(CaSO_4)$ to cements to increase aluminate and sulfate concentrations, resulting in extensive value [Ca₆Al₂(SO₄)₃(OH)₁₂•26H₂O] crystals on such hydration [40]. Traditional shrinkage-compensating cements, on the other hand, are inappropriate for massive structural parts where shrinkage is often detected as a product of cooling after a preliminary exergonic hydration reaction instead of autogenous or dried shrinkage of the cement hydrates—as shrinkage occurs far after the intended expansive materials have developed. MgO-extensive cements have been gaining popularity for this reason. The extensive hydration of MgO to Mg(OH)₂, which results in a 117 percent molar solid mass transfer, is used in these studies [41–43]. One study was conducted to investigate the mechanical and morphological properties of carbonized corn stalk used to reinforce polyester composites in the manufacture of environmentally friendly composites [32]. A comparison of the results reveals two important findings. For starters, agro-waste materials could be employed in their natural state in reinforcing applications, such as bamboo in cementitious applications. Second, the agro-waste materials might be treated or employed as chemical admixtures in reinforcing biocomposites, implying that they needed to be treated before being used in reinforcement applications [32,44,45].

The sustainability advantages of MgO involve (i) adequacy of carbonate to gain vigor/strength in relation to this, (ii) appreciable durability increase due to the higher resistance of the hydration and carbonation products in assailant environments, (iii) lower susceptibility to smudginess enabling the utilization of considerable amounts of waste and industrial by-products, and (iv) probable entirely recyclable where MgO is used alone as the binder as its carbonation time course produces magnesium carbonates, which are the dominant resource for the production of magnesia. Interchangeably, accurate restrictions come into being concerning the production and application of MgO cements in the construction sector [43].

2.4. Recent Developments for Building Design

A common thread running through these research studies is that they all aim to solve two major problems. The first is to reduce the impact of the construction industry on climate change by promoting the use of alternative materials. The implication of the two factors (depletion of non-renewable resources, high pollution levels) makes it necessary to refocus on the need for sustainability in the construction industry. On the one hand, it is necessary to ensure that the raw materials used in construction, such as cement and sand, are not used up, but on the other hand, it is also necessary to ensure that the results of the construction industry (buildings and infrastructure) do not emit significant amounts of carbon dioxide. As a result, several efforts, as well as countless research studies, have been developed over the years to ensure the sustainability of the construction sector [32,44].

Another industrial hurdle is the pre-processing stage that some agricultural wastes must undergo before they can be combined with conventional materials. In one study, wheat and barley straw fibers were treated with boiling water and linseed oil to reduce water absorption while improving binder compatibility and adhesion; they were used to produce lightweight composites for building insulation. In another study, alkali was used to treat agricultural waste in the development of composite materials made of rice straw, magnesium cement adhesive, and a foaming agent (NaOH) [32]. Similarly, researchers were observed burning other solid wastes such as peanut, rice, and barley husks to produce ash that could be mixed with traditional materials for the construction of bricks and masonry components. It was also found that the ash had to be further sieved before being incorporated into the bricks [44].

It is very well known that the incorporation of a low amount of short fibers (Figure 3) into the cementitious matrix is a very effective solution for preventing brittleness and improving the tensile ductility of PC-based composite materials [45]. Engineered cementitious composites (ECC), which adopt polymeric fibers at a typical 2% by volume mixture, are a good example of effective and successful fiber supplements. ECC shows strain-hardening behavior like metal, and thus, the tensile stress of these types of composites continue to increase even within the presence of cracks. Cracking is considered one of the most common forms of deterioration in concrete structures leading to strength loss, thermal discomfort, and energy consumption. Cracks in buildings are inevitable and can be created at nearly every phase of the material's service life by thermal gradients, over-loading, or chemical attacks.

The high cement content is required to produce ECC mixes for providing strain hardening behavior and reducing the matrix toughness. These characteristics of ECCs offer an attractive change for utilization of reactive MgO cement combined with CO₂ curing and has encouraged the development of a novel version of ECC built upon the MgO-fly ash-CO₂ system. This innovative MgO-ECC has a tensile strain ductility of more than 5% and successfully sequesters approximately 30% CO₂ by mass of MgO within 24 h, which, in turn, provides new sustainable building design applications for the carbonated MgO cement [44–47].

Wu et al. [43,44] investigated the cracking behavior of concrete made with reactive MgO and flew ash cured with an accelerated carbonating process for one, three and seven days. The study revealed that the carbonation curing densifies the interfacial bonding system, resulting in a significant increase of the retarded tensile strength at first cracking, which in turn, has considerable influence on the fracture properties of concrete. The recently developed ECC-supported reactive MgO-fly ash blends show a guarantee in building up self-healing ability. The typical width of the multiple micro-cracks formed under uniaxial tension measured but 60 μ m. The ECC's matrix contains a high volume of reactive MgO, which is not completely responded to during the accelerated CO₂ carbonation. The unreacted MgO and its hydration products create the potential for subsequent dissolution and precipitation in microcracks that will facilitate the self-healing process [46–48].

Reactive MgO is not only used for self-healing but also frequently used to optimize the shrinkage behavior of concrete. While M92-200 is a moderately reactive grade of MgO that has been used for a variety of applications, researchers have also used highly reactive grades of MgO to reduce shrinkage in concrete [49]. Both reactive MgO types, therefore, have a high potential for self-healing of drying shrinkage cracks. The development of internal stresses within the cement matrix is caused by the expansion of MgO in the early stages of hydration. The reason for equalizing the shrinkage stress in cement is well known. The optimum proportions of MgO in PC lead to suitable expansion by densification of the microstructure through partial MgO hydration.



Figure 3. Structure of short and long fibers controlling micro-cracks and their influence on the stress–crack opening curve. Reprinted with permission from Ref. [48]. Copyright 2019 Elsevier.

The conversion of lignin to high value-added products plays a key role in the economic viability of a biorefinery. For example, some potential new applications for lignin are the production of nano-scale structures for metal absorption captured in water or air pollutant; generation of inexpensive-effective pyrolysis processes to obtain simple compounds as industrial solvents to replace petroleum-derived compounds such as toluene, xylene, and benzene; or development of 3D printing materials designed for biomedical applications (artificial tissues as support for antioxidant, antimicrobial, or biodegradable compounds from lignin). Optimizing the catalytic mechanisms using lignin as raw material will facilitate the development of improved sustainable materials [46].

In a concert of emerging strategies countering such deterioration, the self-healing of concrete cracks has been progressively contemplated. Although the addition of fiber was shown to have a positive effect in reducing water permeability, increasing compressive and flexural strengths of matrixes, controlling micro-cracks, and improving impact resistance—the improvement was far from ideal to solve the mechanical and durable issues that MOC encounters in practical applications [46,48].

2.5. Life Cycle Assessment for Building Design

The demand for cement is constantly increasing, due to the growth of the world population, making it the most used building material, reaching a production of 10 billion tons per year. Because of these huge quantities, the impact on the environment is substantial in terms of embodied energy consumption, raw materials required, and greenhouse gas emissions. Indeed, the latter aspect amounts to around 5–7% of the anthropogenic carbon dioxide emitted, contributing to global warming, mostly because of the Portland cement, one of the widely used binders of modern concrete mixtures, which is not environmentally friendly [49].

A building's total life cycle energy consumption is divided into two categories: embodied energy and operational energy. Embodied energy is the entire quantity of nonrenewable primary energy necessary for all direct and indirect processes associated with the construction of a building, maintenance, and end-of-life, whereas operational energy is the energy used during the building's use stage [50]. To reduce carbon dioxide emissions, the architectural industry has concentrated on reducing the usage of fossil fuels throughout the construction stage. However, in order to achieve the net-zero policy target, efforts must be made to decrease the embodied energy that is generated during the collection and production of building materials. Nevertheless, even in the case of green and sustainable architecture, which basically aims to minimize carbon dioxide emissions and environmental impacts over the life cycle, building foundations or structural frames are mostly made of concrete, which requires a lot of energy during the manufacturing process. This is because of the difficulties in developing viable alternatives to the current concrete-based strategy when numerous considerations like structural safety and economic efficiency are considered. As a result, developing a new binder that is more environmentally friendly and reduces the embodied energy of concrete could be a useful alternative to finding a construction method that substitutes concrete foundations [51].

There are over 100,000 materials in our world, and suitable material selection is critical. Different factors can be considered to select alternative materials, depending on the required functional properties and the final cost. Today, more attention must be devoted to sustainability. Sustainable materials can be defined as materials derived from renewable resources. They must have a zero/minimal impact on the environment and society for their extraction and production. Examples are recycled metals, bio-based polymers, and materials for renewable energy. In some cases, biomaterials can be interesting for combined applications, such as bioremediation and fuel production [49]. There are also eco-friendly binders that lead to less carbon dioxide emissions than OPC, namely including magnesium phosphate cement, geopolymer, alkali-activated slag cement, and super sulfate cement [51–60].

Sinka et al. [61] developed a bio-based wall panel consisting of MgO cement (as a binder) and hemp shives and compared its CO_2 emission performance to the other wall panels made with traditional materials. Figure 4 illustrates that the emissions of a wooden frame wall, which is filled with the mineral wool, emits only 16.1 kg/CO₂ eq m², 27% more CO_2 of the magnesium-hemp panel, as both wall types consist of a load-bearing wooden frame, the largest part of emissions (around 50%) comes from the mineral wool. More interestingly, the magnesium-hemp material produces significantly fewer emissions compared to the traditionally used materials because hemp shives could absorb the CO_2 that was built in the wall material.

A recent study conducted by Li et al. [60] investigated a life cycle assessment (LCA) of an innovative and sustainable magnesium oxide structural insulated sandwich panel (MgO SIP) used for a high-performance smart home in Vancouver. For those purposes, the authors constructed a prototype house (Figure 5) and compared the environmental impacts across six parameters for the MgO SIPs, traditional SIPs, and traditional stick-frame construction across the life cycle phases of raw material extraction, manufacturing, transportation, construction, and operation. The findings of this study indicated that the MgO SIPs do not outperform conventional alternatives, notably because of the long-distance transportation of materials. However, further LCA of hypothetical scenarios shows that MgO SIPs have a great potential to become more environmentally friendly than the conventional alternatives by sourcing MgO domestically, implementing onsite manufacturing, and eliminating oriented strand boards.



Figure 4. (a) Comparison of different wall types and their greenhouse grass emissions; (b) emissions by percentage of hemp-magnesium panel parts. Reprinted with permission from Ref. [61]. Copyright 2018 Elsevier.



Figure 5. The prototype structure for the study. Reprinted with permission from Ref. [60]. Copyright 2018 Elsevier.

3. Conclusions

Research on MgO and MgO-based cementitious composites is very important nowadays when most of the CO₂ emission and heat consumption is made for heating and cooling purposes in buildings. MgO-based building elements (for example, wall panels, roof decking) can effectively be used for energy harvesting in buildings and provide a comfortable temperature inside the building. This study refers to the characteristics and developments of MgO-based composites.

• MgO-based composite application in cementitious materials and energy-efficient buildings, and summaries of the numerical and experimental studies on these mate-

rials, have shown that MgO cement-based composites can play an important role in terms of sustainable and environmentally friendly building design.

- It has been emphasized in studies that MgO-based composites can provide increases in temperature comfort in buildings.
- It is very important that MgO, which has been recently used in buildings with a wide variety of methods, is suitable for climatic conditions, and the type of application should be selected according to the climate.
- It's crucial to form an oxidation and reduction method that can remove individual carbon stratum and isolate them without changing their composition until magnesium oxide can be used as an intermediate in the development of a monolayer or few-layer MgO sandwich panel parts.
- It has been observed that although chemical reduction of magnesium oxide is generally thought to be the best process for mass production of MgO composites, scientists have struggled to complete the challenge of manufacturing lightweight and fiber-reinforced MgO sheets of the same quality as mechanical exfoliation, but on a much larger scale.
- We should expect magnesium to become much more commonly used in consumer and industrial applications until this problem is resolved.
- Finally, MgO-based engineered cementitious modified sustainable building materials provide crack toughening mechanisms improving the bridging stress of the cementitious matrix and make the micro-structure much denser, which, in turn, increases the load-carrying capacity of the composite under mechanical stresses.

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References

- 1. Freedonia Group. *World Construction Aggregates- Demand and Sales Forecasts, Market Industry Study No.3389*; Freedonia Group: Cleveland, OH, USA, 2016; p. 390.
- 2. USGS. Commodity Statistics and Information Mineral. Yearbooks; USA Geological Survey: Washington, DC, USA, 2015.
- 3. Marinković, S.; Radonjanin, V.; Malesev, M.; Ignjatovic, I. Comparative environmental assessment of natural and recycled aggregate concrete. *Waste Manag.* **2010**, *30*, 2255–2264. [CrossRef]
- 4. De Schepper, M.; Heede, P.; Driessche, I.; de Belie, N. Life cycle assessment of completely recyclable concrete. *Materials* **2014**, *7*, 6010–6027. [CrossRef] [PubMed]
- 5. Kurda, R.; de Brito, J.; Silvestre, J.D. Combined economic and mechanical performance optimization of recycled aggregate concrete with high volume of fly ash. *Appl. Sci.* **2018**, *8*, 1189. [CrossRef]
- 6. Kurda, R.; de Brito, J.; Silvestre, J.D. Water absorption and electrical resistivity of concrete with recycled concrete aggregates and fly ash. *Cem. Concr. Compos.* **2019**, *95*, 169–182. [CrossRef]
- Berndt, M.L. Properties of sustainable concrete containing fly ash, slag and recycled concrete aggregate. *Constr. Build. Mater.* 2009, 23, 2606–2613. [CrossRef]
- 8. Kou, S.C.; Poon, C.S.; Agrela, F. Comparisons of natural and recycled aggregate concretes prepared with the addition of di erent mineral admixtures. *Cem. Concr. Compos.* 2011, *33*, 788–795. [CrossRef]
- 9. Ferdous, W.; Manalo, A.; Wong, H.; Abousnina, R.; Ajarmeh, O.; Zhuge, Y.; Schubel, P. Optimal design for epoxy polymer concrete based on mechanical properties and durability aspects. *Constr. Build. Mater.* **2020**, 232, 117–229. [CrossRef]

- 10. Canterford, J.H. Magnesia—An important industrial mineral: A review of processing options and uses Miner. *Process. Extr. Metall. Rev.* **1985**, *2*, 57–104. [CrossRef]
- 11. Eubank, W.R. Calcination studies of magnesium oxides. J. Am. Ceram. Soc. 1951, 34, 225–229. [CrossRef]
- 12. Wright, J.M.; Colling, A. Seawater: Its Composition, Properties and Behaviour, 2nd ed.; Elsevier Science: Oxford, UK, 1995.
- Seeger, M.; Otto, W.; Flick, W.; Bickelhaupt, F.; Akkerman, O.S. Magnesium compounds. In Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000.
- 14. Mo, L.; Deng, M.; Tang, M.; Al-Tabbaa, A. MgO expansive cement and concrete in China: Past, present and future. *Cem. Concr. Res.* **2014**, *57*, 1–12. [CrossRef]
- 15. Venkatarama Reddy, B.V. Sustainable materials for low carbon buildings. Int. J. Low Carbon Technol. 2009, 4, 175–181. [CrossRef]
- 16. Vance, K.; Falzone, G.; Pignatelli, I.; Bauchy, M.; Balonis, M.; Sant, G. Direct Carbonation of Ca(OH)₂ Using Liquid and Supercritical CO₂: Implications for Carbon-Neutral Cementation. *Ind. Eng. Chem. Res.* **2015**, *54*, 8908–8918. [CrossRef]
- 17. Bontempi, E.; Sorrentino, G.P.; Zanoletti, A.; Alessandri, I.; Depero, L.E.; Caneschi, A. Sustainable materials and their contribution to the sustainable development goals (SDGs): A critical review based on an Italian example. *Molecules* **2021**, *26*, 1407. [CrossRef]
- Snellings, R.; Mertens, G.; Elsen, J. Supplementary Cementitious Materials. *Rev. Mineral. Geochem.* 2012, 74, 211–278. [CrossRef]
 Lang, E. Blast furnace cements. In *Structure and Performance of Cements*, 2nd ed.; Bensted, J., Barnes, P., Eds.; Spon Press: London,
- UK, 202; pp. 310–325.
 Sonchi M. Ammer V. Diodonich P. Systeinability of compute conductor and computerent condector and computerent conductor.
- Sonebi, M.; Ammar, Y.; Diederich, P. Sustainability of cement, concrete and cement replacement materials in construction. In Sustainability of Construction Materials; Woodhead Publishing: Oxford, UK, 2016; pp. 371–396.
- 21. Gosselin, C.; Scrivener, K. Microstructural Development of Calcium Aluminate Cement-Based Systems with and without Supplementary Cementitious Materials; EPFL: Lausanne, Switzerland, 2009; p. 234.
- 22. Walling, S.A.; Provis, J.L. Magnesia-Based Cements: A Journey of 150 Years, and Cements for the Future? *Chem. Rev.* 2016, 116, 4170–4204. [CrossRef]
- 23. Sodangi, M.; Kazmi, Z.A. Integrated evaluation of the impediments to the adoption of coconut palm wood as a sustainable material for building construction. *Sustainability* **2020**, *12*, 7676. [CrossRef]
- 24. Vandeperre, L.J.; Liska, M.; Al-Tabbaa, A. Microstructures of reactive magnesia cement blends. *Cem. Concr. Compos.* 2008, 30, 706–714. [CrossRef]
- 25. Cwirzen, A.; Habermehl-Cwirzen, K. Effects of reactive magnesia on microstructure and frost durability of Portland cement–based binders. *J. Mater. Civ. Eng.* 2013, 25, 1941–1950. [CrossRef]
- 26. Jackson, P.J. Portland cement: Classification and manufacture. In *Lea's Chemistry of Cement and Concrete;* Hewlett, P.C., Ed.; Butterworth-Heinemann: Oxford, UK, 2003.
- 27. Vandeperre, L.J.; Liska, M.; Al-Tabbaa, A. Hydration and mechanical properties of magnesia, pulverized fuel ash, and Portland cement blends. *J. Mater. Civ. Eng.* 2008, 20, 375–383. [CrossRef]
- Harrison, J. New cements based on the addition of reactive magnesia to portland cement with or without added pozzolan. In Proceedings of the CIA Conference: Concrete in the Third Millennium, CIA, Brisbane, Australia, 17–19 July 2003.
- 29. Vandeperre, L.J.; Al-Tabbaa, A. Accelerated carbonation of reactive MgO cements. Adv. Cem. Res. 2007, 19, 67–79. [CrossRef]
- 30. Mo, L.; Panesar, D.K. Effects of accelerated carbonation on the microstructure of Portland cement pastes containing reactive MgO. *Cem. Concr. Res.* **2012**, *42*, 769–777. [CrossRef]
- 31. Maraveas, C. Production of sustainable construction materials using agro-wastes. Materials 2020, 13, 262. [CrossRef] [PubMed]
- 32. Liu, Z.; Wang, S.; Huang, J.; Wei, Z.; Guan, B.; Fang, J. Experimental investigation on properties and microstructure of magnesium oxychloride cement prepared with caustic magnesite and dolomite. *Constr. Build. Mater.* **2015**, *85*, 247–255. [CrossRef]
- Li, Z.; Chau, C.K. Influence of molar ratios on properties of magnesium oxychloride cement. *Cem. Concr. Res.* 2007, 37, 866–870. [CrossRef]
- Abdel-Gawwad, H.A.; Khalil, K.A. Preparation and characterization of one-part magnesium oxychloride cement. Constr. Build. Mater. 2018, 189, 745–750. [CrossRef]
- 35. Bensted, J.; Barnes, P. Structure and Performance of Cements, 2nd ed.; Spon Press: London, UK, 2017.
- 36. Du, C. A review of magnesium oxide in concrete. Concr. Int. 2005, 27, 45-50.
- 37. Bamforth, P.B. In situ measurement of the effect of partial Portland cement replacement using either fly ash or ground granulated blast-furnace slag on the performance of mass concrete. *Proc. Inst. Civ. Eng.* **1980**, *69*, 777–800. [CrossRef]
- 38. Bensted, J. Gypsum in cements. In *Structure and Performance of Cements*, 2nd ed.; Bensted, J., Barnes, P., Eds.; Spon Press: London, UK, 2002.
- 39. Nagataki, S.; Gomi, H. Expansive admixtures (mainly ettringite). Cem. Concr. Compos. 1998, 20, 163–170. [CrossRef]
- 40. Chatterji, S. Mechanism of expansion of concrete due to the presence of dead-burnt CaO and MgO. *Cem. Concr. Res.* **1995**, 25, 51–56. [CrossRef]
- 41. Unluer, C.; Al-Tabbaa, A. Impact of hydrated magnesium carbonate additives on the carbonation of reactive MgO cements. *Cem. Concr. Res.* **2013**, *54*, 87–97. [CrossRef]
- 42. Unluer, C.; Al-Tabbaa, A. Characterization of light and heavy hydrated magnesium carbonates using thermal analysis. *J. Therm. Anal. Calorim.* **2014**, *115*, 595–607. [CrossRef]
- 43. Li, V.; Mishra, D.; Wu, H.-C. Matrix design for pseudo-strain-hardening fibre reinforced cementitious composites. *Mater. Struct.* **1995**, *28*, 586–595. [CrossRef]

- 44. Li, V.C.; Wang, S.; Wu, C. Tensile strain-hardening behavior of polyvinyl alcohol engineered cementitious composite (PVA-ECC). *Mater. J.* **2012**, *98*, 483–492.
- 45. Mo, L.; Panesar, D.K. Accelerated carbonation—A potential approach to sequester CO₂ in cement paste containing slag and reactive MgO. *Cem. Concr. Compos.* **2013**, *43*, 69–77. [CrossRef]
- 46. Vásquez-Garay, F.; Carrillo-Varela, I.; Vidal, C.; Reyes-Contreras, P.; Faccini, M.; Mendonça, R.T. A review on the lignin biopolymer and its integration in the elaboration of sustainable materials. *Sustainability* **2021**, *13*, 2697. [CrossRef]
- 47. Siddique, R.; Naik, T.R. Properties of concrete containing scrap tire rubber-an overview. *Waste Manag.* 2004, 24, 563–569. [CrossRef]
- Wang, Y.; Wei, L.; Yu, J.; Yu, K. Mechanical properties of high ductile magnesium oxychloride cement-based composites after water soaking. *Cem. Concr. Compos.* 2019, 97, 248–258. [CrossRef]
- 49. Forero, J.A.; Bravo, M.; Pacheco, J.; de Brito, J.; Evangelista, L. Fracture Behaviour of Concrete with Reactive Magnesium Oxide as Alternative Binder. *Appl. Sci.* 2021, 11, 2891. [CrossRef]
- 50. Abouhamad, M.; Abu-Hamd, M. Life Cycle Environmental Assessment of Light Steel Framed Buildings with Cement-Based Walls and Floors. *Sustainability* 2020, 12, 10686. [CrossRef]
- 51. Kim, H.-S.; Kim, I.; Yang, W.-H.; Moon, S.-Y.; Lee, J.-Y. Analyzing the Basic Properties and Environmental Footprint Reduction Effects of Highly Sulfated Calcium Silicate Cement. *Sustainability* **2021**, *13*, 7540. [CrossRef]
- 52. Skalny, J.; Skalny, J.P.; Odler, I. *Materials Science of Concrete: Calcium Hydroxide in Concrete;* Wiley-Blackwell: Hoboken, NJ, USA, 2001.
- 53. Wagh, A.S. *Chemically Bonded Phosphate Ceramics: Twenty-First Century Materials with Diverse Applications;* Elsevier: Amsterdam, The Netherlands, 2016.
- 54. Roy, D.M. New strong cement materials: Chemically bonded ceramics. Science 1987, 235, 651–658. [CrossRef] [PubMed]
- 55. Provis, J.L.; Van Deventer, J.S.J. *Geopolymers: Structures, Processing, Properties and Industrial Applications*; Elsevier: Amsterdam, The Netherlands, 2009.
- 56. Davidovits, J. *Geopolymer Chemistry and Applications*, 3rd ed.; Davidovits, J., Ed.; Geopolymer Institute: Saint-Quentin, France, 2011.
- 57. Roy, D.M. Alkali-activated cements opportunities and challenges. Cem. Concr. Res. 1999, 29, 249–254. [CrossRef]
- 58. Shi, C.; Roy, D.; Krivenko, P. Alkali-Activated Cements and Concretes; CRC Press: Boca Raton, FL, USA, 2006.
- 59. Woltron, G. The Utilisation of GGBFS for Advanced Supersulfated. World Cem. Mag. 2009, 10, 157–162.
- 60. Li, P.; Froese, T.M.; Cavka, B.T. Life Cycle Assessment of Magnesium Oxide Structural Insulated Panels for a Smart Home in Vancouver. *Energy Build.* 2018, 175, 78–86. [CrossRef]
- 61. Sinka, M.; Korjakins, A.; Bajare, D.; Zimele, Z.; Sahmenko, G. Bio-based construction panels for low carbon development. *Energy Procedia* **2018**, 147, 220–226. [CrossRef]