

Magnesia as Alternative Binder

Subjects: Others

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Magnesia, or Magnesium oxide (MgO), is a white hygroscopic solid mineral that occurs naturally as periclase and is a source of magnesium. It has an empirical formula of MgO and consists of a lattice of Mg²⁺ ions and O²⁻ ions held together by ionic bonding.

Magnesia is mainly produced by the calcination of magnesium carbonate. Calcining at different temperatures produces magnesia of different reactivity.

The use of reactive MgO as binder in cementitious materials has its advantages and disadvantages.

Keywords: magnesia ; magnesium oxide ; reactivity ; cementitious materials ; literature review ; concrete ; alternative binder ; properties

1. Introduction

The demand for cement and natural aggregates has been exponentially increasing due to rapid construction development. In fact, in 2014, about 40 billion tonnes of aggregates and 4 billion tonnes of cement were required in the construction sector worldwide ^{[1][2]}. Consequently, a significant amount of carbon dioxide (CO₂) is released to the air during the production stage of these materials. For example, to produce 1 tonne of cement it is necessary to use 125 kW of electricity and to emit about 0.89 tonnes of CO₂ emissions to the atmosphere ^{[3][4]}. One way to overcome this issue is by incorporating sustainable materials, such as fly ash (FA), silica fume, slag, metakaolin, and recycled aggregates in concrete ^{[5][6][7][8][9][10]}.

Another alternative approach towards sustainable concrete is through MgO incorporation. Cements with high MgO content gained significant popularity in the last decade, mainly due to the growing concern about climate changes, that is, with the intention and the need to mitigate the CO₂ emissions associated with the production of conventional Portland cements. Some authors believe that it is possible to produce such cements, with a high MgO content, with reduced CO₂ emissions ^[11]. Other authors even believe that it is possible to produce cement that has a positive CO₂ balance, by capturing atmospheric CO₂ to form magnesium minerals (carbonates and hydroxycarbonates). The carbonation of MgO can be described, in general, as the formation of magnesite from MgO, through the absorption of carbon dioxide ^[11].

The utilization of MgO can, in some conditions of calcination and reactivity, decrease the thermal shrinkage ^{[12][13]}, reduce the cost of concrete by decreasing costly cooling measures, and accelerate construction process speed by continuously casting concrete without needing as many cold joints ^[14]. However, the main motivation for the development and upscaling of MgO-based cements was that of an environmental nature. The lower temperatures required for the production of MgO compared to those required for the conversion of CaCO₃ into ordinary Portland cement (OPC) and the energy savings associated with that reduced temperature led many to envision MgO-based cements as central to the future of environmentally friendly cement production. Likewise, MgO's ability to absorb CO₂ from the atmosphere to form a variety of carbonates and hydroxycarbonates fits well into the discussion of "carbon neutral" cements, which could absorb almost as much CO₂ during its lifetime as that emitted during their manufacture. These two interconnected aspects have led to a recent rise in interest, both academic and commercial, in the area of MgO-based cements.

Currently, research has been focusing on the mechanical and durability-related properties of cementitious materials with MgO. However, an extensive and critical revision based on MgO characterization and properties of MgO-cementitious materials has not been conducted yet.

2. Magnesia Production and Its Use in Cementitious Materials

The current global production of MgO is 14 million tonnes annually (USGS, 2012), compared with that of OPC of over 2.6 billion tonnes, with current costs of around ~£200/tonne for reactive MgO (calcined), compared to ~£70/tonne for OPC. The cement production process implemented in most industries is known as the dry process and consists mainly of the following steps: grinding and homogenization of raw materials (obtaining raw flour); clinkerization of the raw flour in rotary kilns (clinker production); subsequent clinker cooling; grinding of clinker and addition of gypsum to obtain cement; bagging and shipping of the final product. This process requires high energy consumption and, since it requires temperatures of up to 1400 °C, it emits a large amount of polluting gases. In turn, magnesia (magnesium oxide, MgO) is mainly produced from the calcination of magnesite in a process similar to the production of lime from limestone. A smaller proportion of the world's MgO production comes from seawater and brine sources, or other sources [15].

2.1. Calcination of Magnesite

The most common method used for MgO production is the calcination of magnesite ($\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$) because of the higher energy requirements for production through the wet route. To produce 1 tonne of MgO from fully decomposed pure magnesite, about 1.08 tonnes of CO₂ can be generated, while OPC production results in 0.85 tonnes of CO₂ [16][17]. However, the amounts of CO₂ released and MgO produced are highly dependent on the temperature and CO₂ pressure used. A kiln with variable temperature is used for magnesite calcination, depending on the required MgO reactivity. In general, four types of MgO are produced [15][16]: light-burned or caustic-calcined MgO (calcined at 700–1000 °C), with the highest reactivity and greatest specific surface area; hard-burned MgO (calcined at 1000–1500 °C), with lower reactivity and specific surface area than those of light-burned MgO; dead-burned MgO or periclase (calcined at 1400–2000 °C), with the lowest specific surface area, making them almost unreactive; fused MgO (calcined at 2800 °C) with the lowest reactivity.

2.2. Calcination of Magnesium Hydroxide

Calcining magnesium hydroxide includes heating a filter cake containing 50–72% magnesium hydroxide solids ($\text{Mg}(\text{OH})_2 + \text{Heat} \rightarrow \text{MgO} + \text{H}_2\text{O}$). This procedure is similar to that of MgO production in either a brine or seawater process. After placing the filter cake in a kiln, the decomposition reaction starts to take place at 350 °C and it quickly increases above this temperature. During this calcination, several inconsequential processes occur, including filter cake dehydration, dry magnesium hydroxide decomposition, and MgO sintering. The removal of chemically bound water from magnesium hydroxide is a difficult process without raising the temperature above 1000 °C [18].

2.3. Seawater and Brine

MgO can be produced from alkaline precipitation of brucite ($\text{Mg}(\text{OH})_2$) from seawater or Mg rich brine. In the former method, Mg concentration is about 1.4 g/L [19]. The seawater is pre-treated with sulphuric acid to reduce the pH to 4 to remove the carbonates ($\text{Ca}(\text{HCO}_3)_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4\text{CO}_2 \uparrow + \text{H}_2\text{O}$). Then, an alkali (lime or sodium hydroxide) is added to raise the pH above the brucite precipitation point (pH 10.5). Sodium hydroxide is used to obtain MgO with low Ca content ($\text{CaO} + \text{H}_2\text{O} + \text{MgCl}_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaCl}_2$). Lime from dolomitic limestone is used to reduce the required additive quantity ($\text{CaO} + \text{MgO} + 2\text{H}_2\text{O} + \text{MgCl}_2 \rightarrow 2\text{Mg}(\text{OH})_2 \downarrow + \text{CaCl}_2$). After brucite slurry filtration, the filter cake obtained is decomposed at temperatures above 350 °C, requiring higher energy than that of the magnesite calcination method.

Another MgO production method is by carbonation, involving CO₂ sequestration through carbonating Mg rich solutions [19][20][21]. For this purpose, natural (seawater or brine) or waste-based solutions (water from oil extraction, rejected brines from a desalination process) are used. The reaction between Mg²⁺ and CO₂ sparged in the solution leads to the precipitation of Mg carbonate. The Mg carbonate type produced depends on the CO₂ pressure and temperature [20]. For example, the formation of hydrated magnesium carbonates (nesquehonite and hydromagnesite), and magnesite occurs at temperatures of 25 °C, 120 °C and 120 °C, and CO₂ pressures of 1 bar, 3 bar, and 100 bar, respectively. After that, the obtained Mg carbonate is calcined to formulate MgO.

2.4. Extraction of Magnesia from Mg-Bearing Minerals

This method involves geological CO₂ sequestration, where rocks containing chemical groups capable of carbonation are decomposed to suitable precursors to react with CO₂ [22][23][24]. The magnesium silicates decomposition can be facilitated by various methods. The first one is through Mg silicate acid digestion ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4(\text{s}) + 6\text{HCl}(\text{aq}) \rightarrow 3\text{MgCl}_2(\text{aq}) + 2\text{SiO}_2(\text{s}) + 5\text{H}_2\text{O}(\text{l})$), followed by brucite precipitation ($\text{MgCl}_2 + 2\text{NaOH} \rightarrow \text{Mg}(\text{OH})_2 + 2\text{NaCl}$), and its calcination ($\text{Mg}(\text{OH})_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$) [22]. The second method is through Mg silicate carbonation with subsequent Mg carbonate calcination ($(\text{Mg}, \text{Ca})_x\text{Si}_y\text{O}_{x+2y} + x\text{CO}_2 \rightarrow x(\text{Mg}, \text{Ca})\text{CO}_3 + y\text{SiO}_2$) [24]. The Mg

carbonate type from this process depends on the CO₂ pressure and temperature. For example, formulation of magnesite occurs at 155 °C and 126 bar, and hydrated magnesium carbonates at lower temperature and pressure [24]. After that, the carbonates would be calcined to produce MgO, CO₂ and possibly H₂O.

2.5. MgO in Cementitious Materials

In general, two main methods are used to add MgO in cementitious materials. One is by increasing the periclase (magnesium oxide mineral) content in cement clinker to produce high magnesia cement. This method has been used in dam concrete for about 40 years in China [25]. The second method is by preparing MgO from magnesite (MgCO₃) calcination and then incorporating the material in concrete as an expansive additive [25]. When using the second method, it is important to homogeneously disperse MgO in concrete by using an adequate mixing process to avoid heterogeneous expansion that could lead to concrete destruction.

The addition of MgO to conventional Portland cements results in the formation of Mg(OH)₂ ($\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2$) and its subsequent carbonation ($\text{Mg}(\text{OH})_2 + \text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), giving rise to hydrated magnesium carbonates. This type of cement was designed to replace Portland cement in large quantities, thereby deriving environmental benefits with respect to CO₂ emissions. However, due to the long-term dimensional instability seen in concrete with cements with high MgO content, existing standards strictly limit the MgO content that can be used in Portland cements [11].

3. Conclusions

The following main conclusions were drawn:

- The compressive strength, flexural strength and tensile strength of cementitious materials decreased with the incorporation and increase in the MgO content, regardless of the material being added directly to the mix or to the cement clinker. This was mainly attributed to the porosity increment and lower hydration of the MgO mixes, when compared to conventional mixes without MgO. The reactivity of MgO showed insignificant influence on the strength of cementitious materials;
- The incorporation of MgO could lead to porosity decrease, when compared to that of conventional reference mixes, under accelerated carbonation. By contrast, porosity increased with the addition of MgO under ambient carbonation condition;
- The carbonation of concrete mixes produced with MgO tends to be higher than that of conventional concrete mixes. This trend becomes more evident with higher MgO incorporation levels;
- The chloride ion migration coefficient increased by incorporating MgO in mixes water-cured for 28 days and decreased in those water-cured for 360 days. This decrease was attributed to the reduced porosity with the addition of MgO in mixes cured for 360 days;
- The initial expansion of concrete mixes increased by increasing the MgO content;
- The shrinkage of cementitious materials decreased with the incorporation of MgO due to the compensation of the shrinkage by MgO hydration, during 1–5 days. The shrinkage of cementitious materials fell significantly by increasing the reactivity of MgO;
- The hydration degree of cementitious material mixes was not changed by the addition of MgO, during the first 7 h of mix production. This was attributed to the accelerated formation of C–S–H. However, the addition of MgO led to a decrease of maximum heat flow peak between 7–12 h and increase of heat flow between 12–48 h. The incorporation of hydration agent increased the MgO hydration, while the opposite effect was observed with the addition of dispersion agent, associated with the deflocculating effect of the latter;
- Microscopic analysis showed that cementitious materials produced with MgO may have had denser microstructure when compared to that of conventional reference mixes. This was attributed to MgO hydration products filling the pores and to the expansion effect of MgO.

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