THE ALTERNATIVE REFRACTORY MAGNESIA SOURCES IN THE CONTEXT OF DECARBONIZATION

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ABSTRACT

Magnesia (MgO), a key refractory material, is traditionally produced by calcining magnesite ($MgCO_3$), a process that releases substantial CO_2 and contributes to global warming. As environmental concerns grow, alternative sources of magnesia are gaining attention. Beyond magnesite, it can be derived from seawater, brines, or magnesium silicates via brucite ($Mg(OH)_2$) precipitation and subsequent calcination, with silicates requiring an additional leaching step. While synthetic magnesia avoids direct CO_2 emissions from magnesite, it remains energy-intensive and, depending on the alkali agent and energy source, can have a higher overall carbon footprint. Recent studies on carbonation methods in synthetic magnesia production show promising results for emission reduction. This study, developed within the CESAREF consortium, explores alternative magnesia sources and process optimizations aimed at decarbonizing magnesia production. The findings offer insights into more sustainable practices for the refractory industry.

INTRODUCTION

Despite its significance in various industries, the majority of magnesium is consumed in its oxide form, magnesia (MgO), which serves as a crucial component in refractory materials. These materials are essential in high-temperature industrial processes such as those used in the production of steel, cement, ceramics, glass, and various non-ferrous metals. As global demand rises in key sectors like energy transition, aerospace, and infrastructure development, the availability and performance of refractories become increasingly important. Notably, there are limited substitutes for magnesia in these applications and no viable alternatives to refractories themselves [1].

Magnesia stands out among refractory oxides for its extremely high melting point (around 2800 °C), as well as its strong resistance to both thermal shock and basic slags. The bulk of magnesia production originates from mineral sources, with magnesite ($MgCO_3$) being the most common. Other sources such as brucite ($Mg(OH)_2$) and carnallite ($KMgCl_3 \cdot 6H_2O$) contribute less significantly [2]. Magnesia derived from magnesite is named natural magnesia, while synthetic magnesia is typically obtained from seawater, brines, and other magnesium-rich sources. However, the latter are not yet competitive in many regions due to economic and technical constraints.

Magnesium is one of the most abundant elements in Earth's crust and is particularly concentrated in ultramafic rock environments. MgO is the second most prevalent oxide in the mantle, making up nearly 38% of its composition [3], while it constitutes about 4.66 wt% of the continental crust [4].

According to the U.S. Geological Survey [5], global magnesite reserves are estimated at 7.7 billion metric tons (in MgO content), with Russia and Slovakia holding the largest shares—2.3 and 1.2 billion metric tons, respectively. In 2024, global production reached 22 million metric tons, with China leading by a wide margin at 13 million metric tons, followed by Russia (2.5 million) and Brazil (1.8 million). Given its strategic role and dependency on external suppliers—especially China—metallic magnesium has been consistently included in all five iterations of the EU's Critical Raw Materials (CRMs) list. Despite its relevance, magnesite was only briefly classified as a critical raw material by the EU in 2014 and was later removed from the list in 2017, as Europe was considered self-sufficient at the time [6,7].

Magnesia production is energy-intensive and associated with high carbon dioxide emissions, primarily due to calcination and the combustion of fossil fuels. Although industry players have been striving to reduce these emissions, progress is hindered by the limited availability of cost-effective Carbon Capture, Utilization, and Storage (CCUS) technologies. As a result, the transition to low-carbon magnesia production remains challenging, particularly within the EU. Exploring alternative, lower-emission production pathways is essential to improving environmental performance and securing future supply.

Magnesia is a vital material in the refractory sector, accounting for over 70% of the industry's raw material base by weight [8]. Refractories are indispensable for industries that rely on high-temperature processes, such as steel, cement, ceramics, glass, and non-ferrous metals. The demand for high-quality refractories is expected to grow steadily due to ongoing industrial development and infrastructure expansion. Additionally, the shift toward decarbonization and electrification in heavy industries places new demands on refractory performance, potentially requiring new formulations and supply chain adjustments.

NATURAL MAGNESIA

To produce dense and stable grains suitable for refractory applications, magnesite must undergo a sintering process. However, this thermal treatment presents a major environmental challenge: during the decomposition of magnesite (Eq. 1), around 50% of its initial mass is released as CO_2—a significant contributor to global warming, which remains a critical global issue [9]. On top of that, additional CO_2 is generated from the combustion needed to heat the process, making magnesia production a highly carbon-intensive operation.

$$MgCO_{3(s)} \overset{\Delta}{\rightarrow} MgO_{(s)} + CO_{2(g)} \tag{1}$$

Magnesia is commercially available in three primary forms: Caustic-Calcined Magnesia (CCM), Dead-Burned Magnesia (DBM), and Fused Magnesia (FM), each with distinct properties and calcination conditions.

CCM is produced at around 800 °C, requiring relatively low energy. However, due to its high reactivity and low strength, it is not suitable for refractory applications. Instead, it is widely used in chemical industries such as agriculture, water treatment, and pharmaceuticals [10]. It also serves as a precursor for metallic magnesium, obtained by reducing CCM with ferrosilicon and a catalyst like CaF_2 at 1200 °C in vacuum, producing magnesium vapors that are condensed, refined, and cast [11].

DBM, or sintered magnesia, is produced by firing magnesite or CCM at 1800–2200 °C, resulting in recrystallized grains with low LOI, high density (3.25–3.45 g/cm³), and improved strength. Grain sizes typically range from 50 µm to 200 µm, making DBM a standard refractory aggregate [12].

FM requires the highest energy input. Using electric arc furnaces like the Higgins furnace at over 2800 °C, it produces the largest (400–3,000 µm), densest (3.43–3.54 g/cm³), and most stable magnesia grains, regarded as premium refractory material [13].

Figure 1 shows the world magnesia production by type.

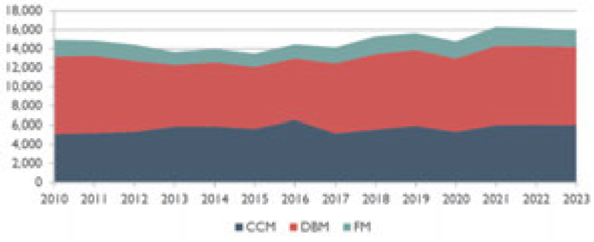

Figure 1 - World MgO production by type [1]

Zhao et al. (2022)[14] assessed the carbon footprint associated with the production of natural magnesia in China. Their findings report emission ranges of 1.440–2.221 kg CO_2eq/kg for CCM, 2.151–3.604 kg CO_2eq/kg for DBM, and 3.937–4.804 kg CO_2eq/kg for FM. To reduce these values, the authors suggest transitioning from coal-fired electricity to nuclear power and replacing natural gas with hydrogen as fuel sources.

SYNTHETIC MAGNESIA

In addition to mineral sources, seawater represents a vast and nearly inexhaustible commercial source of high-purity magnesia. Magnesium is the second most abundant dissolved cation in seawater, with a typical concentration of approximately 1290 ppm [15]. Seawater, along with brines and salt deposits, can also serve as a feedstock for metallic magnesium production via electrolysis. This process involves molten magnesium chloride, which is electrolyzed at temperatures between 655 °C and 720 °C, yielding molten magnesium and chlorine gas. The magnesium is then cast into ingots for subsequent use, while the chlorine by-product can be recovered and sold, particularly for applications in polymer manufacturing [11].

In addition to seawater, other alternative sources for magnesia production include evaporitic deposits, brine effluents from desalination facilities, and saline wastewater generated during oil and gas extraction. One method for producing MgO from seawater begins with a pre-treatment step using sulfuric acid to lower the pH and eliminate carbonate species (Eq. 2). Following this, lime or sodium hydroxide is added to increase the pH beyond the brucite precipitation point (Eq. 3). The resulting brucite slurry is then filtered and subjected to thermal treatment to obtain magnesia-rich raw materials (Eq. 4) [15].

$$Ca(HCO_3)_{2(aq)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(s)} + 2CO_{2(g)} + 2H_2O_{(l)} \quad (2)$$

$$Ca(OH)_{2(aq)} + MgCl_{2(aq)} \rightarrow Mg(OH)_{2(s)} + CaCl_{2(aq)} \quad (3)$$

$$Mg(OH)_{2(s)} \xrightarrow{\Delta} MgO_{(s)} + H_2O_{(l)} \quad (4)$$

Beyond lime and sodium hydroxide, ammonia has also been explored as an alternative alkaline agent for brucite precipitation, as described by Li et al. (2009, 2013)[16,17] and shown in equations 5 and 6. Introducing ammonia gas into a magnesium chloride solution promotes the formation of magnesium hydroxide with a relatively uniform particle size distribution. The morphology of the precipitated particles was found to vary with the operating temperature (20 °C, 40 °C, and 75 °C). Although still at an early stage of development, this method presents potential for reducing the carbon footprint associated with magnesia production.

$$NH_{3(g)} + H_2O_{(l)} \rightarrow NH_4OH_{(aq)} \quad (5)$$

$$MgCl_{2(aq)} + NH_4OH_{(aq)} \rightarrow Mg(OH)_{2(s)} + 2NH_4Cl_{(aq)} \quad (6)$$

Currently, ammonia is most commonly synthesized via the Haber–Bosch process, which is energy-intensive and associated with significant greenhouse gas (GHG) emissions—approximately 2.16 kg CO_2eq per kilogram of ammonia produced—largely due to the need for high temperatures and pressures (30 GJ/t NH_3). Nevertheless, growing efforts are focused on developing lower-carbon alternatives, with green hydrogen-based ammonia production emerging as a particularly promising solution [18].

Synthetic CCM generally has smaller particle sizes and therefore higher reactivity compared to natural CCM. Magnesia produced from seawater and brines can reach higher MgO content and bulk density but requires more energy during production. For instance, producing synthetic DBM through a two-stage firing process can consume up to 60 MkJ/t, which is about four times the energy needed for single-stage burning of DBM from magnesite, and roughly twice the amount required for two-stage burning of DBM made from fine magnesite concentrates [19].

Furthermore, synthetic magnesia derived from seawater contains boron, which negatively impacts its mechanical properties. Although boron content can be lowered to less than 0.01%, this purification process is expensive [13]. Another method to reduce boron is overliming, but excessive use of lime results in higher indirect CO_2 emissions.

Another established method for producing magnesia from seawater and brines is the Aman process. This technique involves feeding a concentrated magnesium chloride solution into a thermal reactor operating between 500 and 600 °C. In this reactor, water vapor reacts with the solution to form magnesium oxide and hydrochloric acid, which is subsequently condensed. The resulting magnesium oxide crystallites are then suspended in slurry to produce magnesium hydroxide, enabling the removal of calcium, sodium, and potassium chlorides. Following filtration and calcination, the process yields highly pure CCM (>99% MgO). However, this method requires more energy compared to conventional magnesia production routes [19].

Authors have demonstrated that MgO can also be produced from seawater and brines through a carbonation process that incorporates CO_2 sequestration by carbonating magnesium-rich solutions. Ferrini et al. (2009)[20] showed that bubbling CO_2 through a solution rich in Mg^{2+} ions results in the rapid precipitation of magnesium carbonates, which can subsequently be calcined to yield MgO, as described in Eq. 1. This carbonation reaction is kinetically favorable and occurs within a short time span.

Mg-bearing minerals

Magnesia production can also be achieved through the decomposition of magnesium-containing minerals [21]. One such approach, described by Teir et al. (2009)[22], involves the acid digestion of magnesium silicates, with serpentine [$Mg_3Si_2O_5(OH)_4$] serving as the magnesium source, as shown in Equation 7. Following the leaching step, the resulting magnesium chloride solution can be treated to precipitate brucite [$Mg(OH)_2$] (Eq. 3), which is then calcined to produce MgO (Eq. 4).

$$Mg_3Si_2O_5(OH)_{4(s)} + 6HCl_{(aq)} \rightarrow 3MgCl_{2(aq)} + 2SiO_{2(s)} + 5H_2O_{(l)} \quad (7)$$

Carbonation presents another pathway to produce MgO directly from Mg-bearing minerals without prior mineral decomposition. Maroto-Valer et al. (2005)[23] demonstrated that carbonation of magnesium silicates, such as serpentine and olivine [$(Mg,Fe)_2SiO_4$], follows the general reaction outlined in Equation 8. However, this method is energy-intensive due to the high pressure (~125 atm) and temperature (~650 °C) conditions required, along with the need for extensive pulverization to increase surface area and facilitate the reaction.

$$(Mg.Ca)_xSi_yO_{x+2y} + xCO_2 \rightarrow x(Mg.Ca)CO_3 + ySiO_2 \quad (8)$$

Maroto-Valer et al. (2005)[23] investigated both physical (hot air and steam) and chemical (acid and base) treatments to activate the surface of Mg-bearing minerals, aiming to increase their surface area and reduce the high costs associated with intensive grinding. Steam activation of serpentine enabled the formation of magnesite at 155 °C and 126 bar, while other hydrated magnesium carbonates could be formed under milder temperature and pressure conditions. The magnesium carbonates produced by these methods can subsequently be calcined to yield MgO, as described previously (Eq. 1).

Carbonation of Mg-bearing minerals offers a promising approach to enhancing the CO_2 value chain, which is a key focus area for reducing the carbon footprint of magnesia production [9,24]. Regarding brucite precipitation (Eq. 3), substituting lime with sodium hydroxide can lower the CO_2 emissions—if NaOH is produced using green electricity—since lime production involves significant CO_2 emissions from both fuel combustion and the release of geogenic CO_2 from limestone.

Utilizing Mg-bearing minerals as an alternative source for MgO production has demonstrated feasibility, yet the approach remains costly due to the significant energy consumption, extensive chemical requirements, and the demanding pressure and temperature conditions involved. Additionally, process efficiency requires improvement, as some carbonation methods—such as steam-activated serpentine—achieve only about 60% conversion to magnesite [23]. These findings suggest that raw materials for magnesia production could potentially extend beyond magnesite to include other magnesium-containing minerals.

ENVIRONMENTAL ANALISYS OF REFRACTORY MgO BY SOURCE

Luong et al. (2018)[25] conducted a comparative analysis of the carbon footprints associated with Chinese MgO production from both synthetic routes (using brines and serpentinite) and natural magnesia, based on Chinese industrial practices. Their findings revealed that the synthetic route, particularly the serpentinite-based process, had the highest carbon footprint, ranging from 3.8 to 7.5 kg CO_2eq/kg MgO. However, the brine-based process showed a footprint of 2.7 to 5.6 kg CO_2eq/kg MgO, which, depending on specific conditions, could be lower than that of natural magnesia (3.1 to 4.5 kg CO_2eq/kg MgO). These results highlight the potential of the brine route to reduce environmental impact compared to other production methods.

Despite its potential, synthetic magnesia production remains more energy-intensive and has a greater environmental impact than the natural route. Shahbaz et al. (2022)[26] performed a cradle-to-gate life cycle assessment (LCA) of synthetic MgO produced from rejected brines in the United Arab Emirates (UAE), evaluating various alkalis. Among the options tested—NaOH, ammonium hydroxide (NH_4OH), and ethanolamine (C_2H_7NO)—lime demonstrated the most favorable environmental performance at the laboratory scale. The study found that raw material extraction and the acquisition of CaO accounted for 74.7% to 83.5% of the total CO_2-equivalent emissions.

Given the growing concern over greenhouse gas (GHG) emissions, synthetic magnesia presents a promising alternative, as its production can involve significantly lower direct CO_2 emissions compared to natural magnesia. However, under the current energy matrix, synthetic magnesia still results in a higher overall CO_2 footprint due to substantial indirect emissions [27]. Expanding the role of synthetic magnesia in global production could contribute to lowering the sector's carbon footprint, but this potential is closely tied to the integration of green electricity in both the magnesia production process and the synthesis of the alkali agent. Achieving this will require not only a reliable and sustainable energy supply but also advancements that enhance the economic competitiveness of synthetic magnesia in terms of cost and production scale.

Table 1 contains a qualitative comparison between the magnesia production routes mentioned in this paper. Note that the classifications are comparative between the given methods.

Table 1 - Qualitative comparison of magnesia production routes

Type	Source	Route	CO_2 footprint	Energy	TRL	Product Quality
Natural	Magnesite	Firing of magnesite (Drnek, 2002)	High[1]	Regular	9	Regular
Synthetic	Seawater	Brucite precipitation (Fontana et al., 2022)	High[2]	High	7	High
		Aman process (Roskill, 2010)	Regular	Very High	7	Very High
		Carbonation (Ferrini et al., 2009)	Regular	High	4	Regular
	Olivine, serpentine	Mineral decomp (Teir et al., 2009)	Regular	Very High	4	Very High
		Direct carbonation (Maroto-Valer et al., 2005)	Regular	Very High	3	Low

1 - CO_2 capture and storage can reduce significantly, with a penalty on readiness.
2 - Conditioned to the use of NaOH or NH_3 (instead of lime) produced with green electricity. Otherwise, it can be even higher than the natural one.

CONCLUDING REMARKS

The urgency in tackling climate change turns the attention of the magnesia industry towards the reduction of CO_2 emissions. In this context, synthetic magnesia could contribute to this goal in the future, but this would require a massive development of green energy production capacity. With the current conditions, the supplies required in the production of synthetic magnesia contribute to increasing the carbon footprint of the final product, leading to higher values than natural magnesia. Therefore, CO_2 capture and storage combined with recycling seem to be the best strategies that could be applied in natural magnesia production to reduce significatively emissions in the near future, requiring minor modifications in the existing facilities.

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