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Proceeding Paper

CO₂ Utilisation in Added-Value Construction Products from Magnesia Production [†]

Guilherme M. D. M. Rubio ^{*} and David Konlechner 

KON Chemical Solutions e.U., Obermüllnerstraße 2A/4/2, 1020 Wien, Austria; david.konlechner@kon-chem.com

^{*} Correspondence: guilherme.rubio@kon-chem.com

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Abstract: In this paper, we propose a solution for the enrichment of CO₂-containing streams from the production of magnesium oxide based on an oxyfuel process for further utilization as raw materials in the carbonation of building materials. A simulation of a specific case in the magnesia industry was investigated and the results were analyzed.

Keywords: magnesium oxide; magnesium carbonate; CO₂-rich off-gas; carbonation; circular economy; CCU; CCS

1. Introduction

The urgent need to address climate change and reduce greenhouse gas emissions has become a global priority [1]. The Paris Agreement, with its aim to limit global warming to well below 2 °C above pre-industrial levels, requires substantial efforts in mitigating carbon dioxide (CO₂) emissions. The European Union has also set ambitious targets to reduce greenhouse gas emissions by at least 55% below 1990 levels by 2030. Achieving these goals necessitates innovative approaches across various industries, particularly those that heavily rely on carbon-intensive processes. The magnesia industry is one such industry facing the challenge of reducing its CO₂ emissions [2]. The direct CO₂ emissions resulting from the thermal decomposition of magnesium carbonate contribute to overall greenhouse gas emissions. Additionally, the steel industry, which is closely linked to magnesia production, emits significant amounts of CO₂ that are often combined with waste slags that hold little market value [3]. This situation intensifies the need to find effective strategies to address emissions from both industries. To tackle this issue, the Carbon4Minerals project under the Horizon Europe programme aims to reduce greenhouse gas emissions from process industries, specifically focusing on the hard-to-abate CO₂ emissions from steel and cement production. By capturing and recycling these emissions, the project aims to unlock a vast stock of resources for low-carbon binders and construction materials, thereby contributing to the reduction of greenhouse gas emissions from the process industry. However, only a few solutions are specifically designed for the magnesia industry. In this report, we explore a redesign of the oxyfuel combustion method, which involves burning fuel with a mixture of pure oxygen and flue gases. This alteration in the combustion process offers several advantages in terms of efficiency, emissions reduction, and process control. The solution combines recycling and purifying CO₂ that is emitted during the production of magnesium oxide, with the purpose of it being reused in the carbonation of new construction materials. Through a simulation of a specific case within the magnesia industry, this study aims to assess the feasibility and potential benefits of this approach in reducing emissions and promoting cross-industry collaboration for sustainable solutions that can be applied across different sectors.



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2. Materials and Methods

To assess the feasibility of our approach, we conducted a simulation of the oxyfuel process integrated into the thermal decomposition of MgCO_3 . This simulation, which is depicted in Figure 1, was performed using HSC:Outotec version 9.8.1.2, incorporating established unit operations and equipment informed by decades of process development [4,5]. To simplify the simulation, we assumed the use of a rotary kiln (with 95% of the magnesium oxide being directly obtained from the furnace and the remaining product being collected in a cyclone). The potential for commercializing the high-purity CO_2 off-gas is the main drive of this process, which is described below.

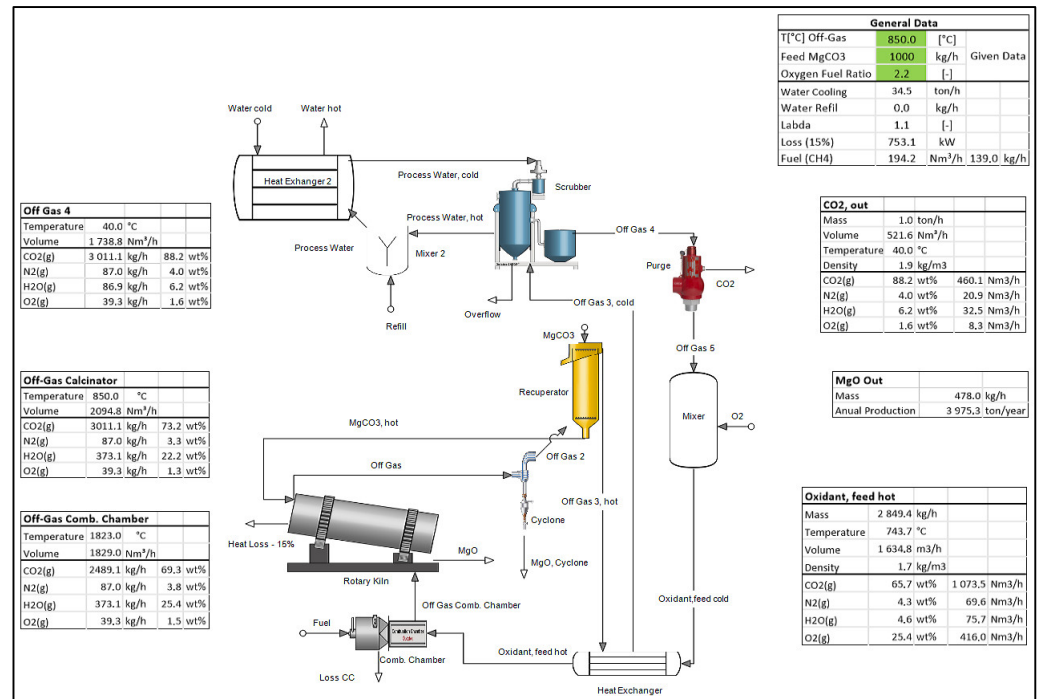


Figure 1. Industrial-style PFD showing the key process equipment used.

In order to simulate this as closely as possible to a real case, the following parameters are assumed for this simulation: 1000 kg/h of MgCO_3 are fed to a recuperator where a stream of hot gas crosses it to heat up the feed material before entering the furnace. A rotary kiln was considered to be a robust solution for the amount we are considering, but a multiple hearth furnace or a fluidized bed could also be considered. The simulation also takes into consideration the furnace temperature, ensuring it is adequate for the thermal decomposition reaction. For this, the amount of CO_2 -rich off-gas purged from the system was defined as 30% together with a defined oxygen–fuel ratio of 2.2 ($\lambda = 1.1$).

In the roasting section, MgCO_3 is thermally decomposed. The temperature is kept as low as possible so as not to form a melt inside the rotary kiln, but it is kept above the 800 °C required for the thermal decomposition reaction. The temperature can be further decreased but at the cost of increasing the amount of O_2 (and N_2) entering the gas mixer section. Natural gas is used as the main fuel source. The connected cyclone allows for the recovery of the remaining material dragged with the off-gas, which is followed by a recuperator that allows for the use of the heat from the off-gas in increasing the MgCO_3 temperature before entering the furnace, thereby decreasing the amount of fuel required to achieve the thermal decomposition temperature.

3. Results

A first heat exchanger is used to recuperate the heat from the off-gas of the furnace (concurrently at 746 °C) to increase the temperature of the oxyfuel stream (rich in CO_2 and

O₂) from 38 °C to 744 °C. This step also decreases the amount of fuel required to achieve the desired temperature in the furnace. The off-gas after the first heat exchanger is at a temperature of 244 °C and contains a high concentration of water. The way to remove the excess water is by decreasing the temperature of the gas stream to a defined dew point. A temperature of 40 °C was chosen to reduce the water concentration in the gas stream from 178 g/m³ to 50 g/m³, thereby ensuring the dryness of the CO₂-rich gas stream. By means of a gas scrubber, cold water enters into contact with the hot gas stream, decreasing the off-gas temperature to 40 °C. Simultaneously, this stream is cooled down using a heat exchanger that pumps cold water (from a nearby water source) at a defined temperature of 22 °C, returning it to 32 °C. This allows the system to cool down without ever contaminating nearby water sources with any particulates or other compounds from the process while keeping the temperature difference of the hot water to a minimum. The CO₂-rich dry gas stream can now be recovered between 15% and 42% of the total off-gas out of the scrubber unit before the temperature inside the furnace is higher than 2000 °C.

The results of our simulation indicate the effectiveness of the first heat exchanger in recuperating heat from the furnace's off-gas, thereby elevating the temperature of the CO₂-rich oxyfuel stream significantly. Additionally, this process reduces the fuel consumption required to reach the desired furnace temperature. However, it is essential to address the presence of water and other impurities in the off-gas to optimize the overall efficiency.

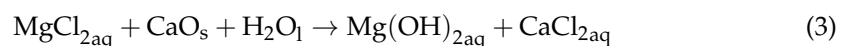
4. Discussion

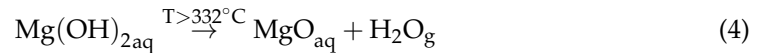
The production of magnesium oxide (MgO) involves the extraction and processing of magnesium-containing minerals, primarily magnesite (magnesium carbonate) or dolomite (a magnesium–calcium carbonate). This process makes up nearly 90% of all magnesia manufactured worldwide, with two other technologies (brine precipitation and serpentine leaching) representing the remaining 10%. For this first technology, the calcination process is the crucial step in the production of magnesia. It involves heating the magnesite or dolomite at high temperatures depending on the type of magnesium oxide required (Equation (1)). Between 1500 °C and 2000 °C periclase (also known as dead-burned magnesium oxide (DBM)) is obtained. It has refractory applications, so it is extensively used in steel production, serving as protective and replaceable linings for furnace kilns and other equipment which have contact with molten steel [6]. Hard-burned magnesium oxide has applications where chemical reactivity is required, and it is produced between 1000 °C and 1500 °C. A third grade of magnesium oxide is obtained at temperatures between 600 and 1000 °C (also known as caustic magnesia), which has several applications in the polymer and paper industry, acid neutralization, among others [7]. Below 700 °C, however, it is reported that CO₂ reabsorption from the off-gas and from the air (when cooled down) can occur due to its increased activity, so the chosen temperature typically has to take into account the chance of increased impurities [8].



Consequently, the sources of CO₂ emissions in the magnesia production process are primarily attributed to the calcination step where direct emissions occur both from fuel combustion and MgCO₃ decomposition to MgO.

Another technology is based on the precipitation of magnesium hydroxide from seawater and brines by using quicklime (see Equations (2)–(4)). The CO₂ source in this case is the formation of quicklime from limestone. Dolomitic limes may also be used, but the process is less common and slightly different.





MgO can also be obtained from serpentines, starting from the leaching of MgCl_2 and consequent calcination to MgO (see Equation (5)).



The last two methods, although not under the scope of this report, are important to mention as in both cases the emissions of CO_2 are comparable to those in the calcination of magnesite case.

When a simple model is used to calculate the CO_2 emissions from the thermal decomposition of MgCO_3 , one can immediately conclude that fuel combustion is the main driver for increased emissions (see Figure 2).

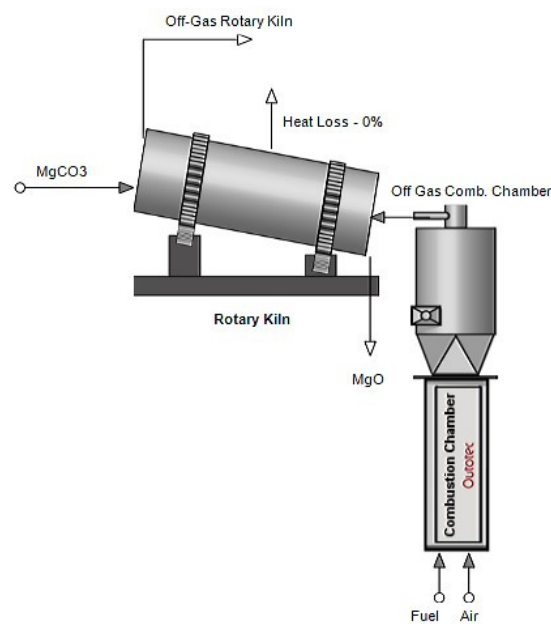


Figure 2. Thermal decomposition of MgCO_3 to MgO with an assumed $\lambda = 1.2$.

The CO_2 emissions from the thermal decomposition of 1000 kg of MgCO_3 at 1000°C with a flame temperature of 1846°C using methane as fuel (CH_4 , 100%) were calculated. Considering the ideal case with a fuel/air ratio of $\lambda = 1.2$ and no losses, as well as a second case with 15% energy losses, the estimated values show that a release of 521 kg of CO_2 occurs from MgCO_3 decomposition. At 0% losses, the combustion of methane releases 255 kg of CO_2 , and at 15% energy loss, 482 kg of CO_2 are estimated to be obtained from methane combustion. Overall, 0.78 kg of CO_2 per kg of MgCO_3 are obtained in the first case, while 1.01 kg of CO_2 /kg of MgCO_3 are obtained in the second case, thereby indicating an increase of 29% in CO_2 emissions per kg of thermally decomposed MgCO_3 (Table 1). For simplicity, indirect emissions from electricity production are not considered in this report.

Table 1. Simulation data for 0% and 15% energy loss in the thermal decomposition of MgCO₃.

Data		0% Energy Loss		15% Energy Loss	
Data	MgCO ₃ Feed	1000	kg/h	1000	kg/h
	Air Factor	11	Nm ³ /Nm ³	11	Nm ³ /Nm ³
	Reactor Temperature	1000	°C	1000	°C
	Volume	1824	Nm ³	3209.1	Nm ³
Composition	CO ₂ (g)	21.7	wt%	15.9	wt%
	N ₂ (g)	61.9	wt%	66.4	wt%
	H ₂ O (g)	14.2	wt%	15.3	wt%
	O ₂ (g)	2.2	wt%	2.4	wt%
	Ratio CO ₂ /MgCO ₃	0.78	kg/kg	1.01	kg/kg

An and Xue (2017) reported several examples based on the standard calcination case. Considering typical fuel (heavy oil, coal, or a mixture of both) for 1000 kg of MgCO₃, the fuel consumptions range between 230 and 250 kg to obtain 90% pure light calcined magnesite (LCM) and between 280 and 300 kg for 94% pure LCM. This results in a direct emission of 1500 kg of CO₂ being emitted for 90% pure LCM and 1650 kg of CO₂ being emitted for 94% pure LCM [9].

Another report, which was undertaken by Luong and coworkers, calculated the carbon footprints of magnesium oxide and magnesium hydroxide (higher than 99% purity) based on two other technologies (brine process and serpentine process) using simulation software, and it carefully compared the calculations with those of previous reports. The direct emissions are, respectively, 2000 and 3400 kg of CO_{2,equiv} per 1000 kg of MgCO₃ for a purity higher than 99%. When taking into consideration the direct emission of CO₂ from the thermal decomposition of MgCO₃ (which does not occur in both the brine and serpentine cases) and the different efficiencies associated with each process, we are left with all three cases having comparable direct emissions [10]. It is clear that the choice of fuel, the energy losses in the entirety of the process, and the quality of magnesium oxide, when they are all combined, contribute to high emissions of CO₂ in the production of MgO.

At present, there are multiple avenues being explored for the purification of CO₂-containing streams from the steel and cement industries with the aim of carbon capture, utilization, and storage. One of these examples was developed by CarbonOrO, which is a partner in the Carbon4Minerals project. CarbonOrO offers an innovative solution where a proprietary amine solvent is used to capture CO₂ from flue gases with a concentration as low as 5%. This high-purity CO₂ stream can then be used for CCUS (carbon capture, utilisation, and storage) and in the upgrade of biogas/landfill gas. Due to the solvent's properties, desorption of CO₂ is possible at temperatures starting at 70 °C, with low energy consumption.

VITO, the project coordinator of the Carbon4Minerals, is currently developing the next generation in carbon capture technology by utilizing the approach of porous structured sorbents where CO₂ gas is selectively captured through a specific sorbent that is packed in several sorption columns. The use of structured porous sorbents instead of classical pellets or granules enables us to lower the energy consumption of the capture process by lowering the pressure drop and improving mass and heat transfer. After adsorption, CO₂ is released in a cyclic way from the sorbent due to the change in pressure and/or temperature to obtain a CO₂-rich stream. Depending on the characteristics of the CO₂ source, CO₂ sorbent materials, such as zeolites, activated carbon, metal-organic frameworks, or amine-functionalised sorbents, can be selected.

Another example is that of the development of a new generation of carbonated materials. The understanding of the mechanisms that regulate the carbonation of natural versus synthetic materials [11] was crucial to investigate carbonation kinetics. De Silva investigated how calcium carbonate microstructures with high strengths can be obtained within hours, in situ, from the lime carbonation process [12]. VITO has perfected the method by developing efficient methods of mineral carbonation and construction materials [13], and

more recently the investigation into the accelerated carbonation of steel slags to produce high-strength construction materials is ongoing [14].

In our discussion, it becomes evident that despite significant developments in emission reduction technologies across other industries, the magnesia sector has received limited attention. Despite the potential benefits of capture, purification, and utilization technologies, their application within this industry remains largely uncharted territory. One solution that tackles the CO₂ emissions in a magnesia case was proposed by KON Chemical Solutions together with Tenova in 2021. The report explores the possibility of substituting the fuel in the serpentine case with pure hydrogen as a method to reduce the direct emissions that arise from fuel combustion [15]. This solution, however, is not focused in the case of magnesite calcination. Finding a solution in its place that recycles or enriches the CO₂-containing off-gas for storage and utilization is crucial since CO₂ is the main by-product of the chemical reaction. With traditional combustion, air is the source of oxygen for the combustion reaction. However, air mainly consists of nitrogen (about 78%) and only contains about 21% oxygen. When fuel is burned in the air, nitrogen dilutes the combustion gases, thereby resulting in a lower concentration of carbon dioxide (CO₂) and water vapour (H₂O). This higher nitrogen content in the flue gases makes capturing and separating CO₂ more challenging. As we have demonstrated, in oxyfuel combustion, the nitrogen content is significantly reduced by using pure oxygen instead of air. By eliminating nitrogen, the combustion process produces a flue gas stream that is mainly composed of CO₂ and H₂O. This stream is highly concentrated, thereby making it easier to capture CO₂ utilizing existent technologies, and the stream is ready to use in some cases.

5. Conclusions

In this report, we demonstrate the feasibility of the enrichment of the flue gas in CO₂ both as a carrier of the oxidizing agent for combustion and also as a purification step yielding a CO₂-rich gas stream containing near 90 wt% CO₂ for storage and utilisation. The process includes two heat recovery steps that allow for the improved efficiency in the thermal decomposition of MgCO₃ into MgO. The off-gas of this process is CO₂-rich, which allows it to be stored (CCS) or used as a raw material in the carbonation of building materials, for example, by pipelining the gas stream to a nearby chemical plant.

Considering the unique properties of magnesia and its potential for CO₂ capture and utilization, there is an opportunity to bridge the gap between the solutions already being developed and the magnesia industry. A possible application of the resulting simulation could be that of the purification of the CO₂-rich gas stream that is obtained from the process. In the real scenario whereby a CO₂-rich stream still contains a high content of impurities (namely water and N₂), it could then be further purified to achieve food-grade quality by utilizing technologies that have already developed by Carbon4Minerals partners. In particular, there is the possibility of the purification of a CO₂ stream that is up to 99% pure, which is based on CarbonOro-developed technology for liquid amines. Another potential solution is based on the technology being developed by VITO by means of a packed column containing porous structured sorbents. There is also the potential for the carbonation of construction materials that do not require high-purity CO₂, which are mainly based on steel slags, together with accelerated carbonation technologies [13,14]. Future research and development efforts could explore the implementation of carbon capture technologies specifically tailored for magnesia production.

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Conflicts of Interest: The authors declare that there are no conflicts of interest regarding this research. The simulation conducted for this study does not involve the use of proprietary or confidential data, and there are no competing financial or personal interests that could influence the objectivity or integrity of the research findings.

References

1. Jones, M.W.; Peters, G.P.; Gasser, T.; Andrew, R.M.; Schwingshackl, C.; Gütschow, J.; Houghton, R.A.; Friedlingstein, P.; Pongratz, J.; Le Quéré, C. National contributions to climate change due to historical emissions of carbon dioxide, methane, and nitrous oxide since 1850. *Sci. Data* **2023**, *10*, 155. [[CrossRef](#)] [[PubMed](#)]
2. An, J.; Li, Y.; Middleton, R.S. Reducing energy consumption and carbon emissions of magnesia refractory products: A life-cycle perspective. *J. Clean. Prod.* **2018**, *182*, 363–371. [[CrossRef](#)]
3. Kim, J.; Sovacool, B.K.; Bazilian, M.; Griffiths, S.; Lee, J.; Yang, M.; Lee, J. Decarbonizing the iron and steel industry: A systematic review of sociotechnical systems, technological innovations, and policy options. *Energy Res. Soc. Sci.* **2022**, *89*, 102565. [[CrossRef](#)]
4. Grohmann, H.; Grill, M. Large-Scale Recovery of High-Purity Magnesium Oxide. DE2107844A1, 9 September 1971.
5. Grohmann, H.; Grill, M. Method for the Large Engineering of Magnesium Oxide High Purity. DE2915129A1, 15 November 1979.
6. Jassim, A.K.; Salmtori, A.S.; Jassam, A.J. Sustainable manufacturing process applied to produce magnesium oxide from sea water. *IOP Conf. Ser. Mater. Sci. Eng.* **2020**, *757*, 012021. [[CrossRef](#)]
7. Chesters, J.H. *Refractories: Production and Properties*; Iron and Steel Institute: London, UK, 1973.
8. Ropp, R.C. The Alkaline Earths as Metals. In *Encyclopedia of the Alkaline Earth Compounds*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2013; pp. 1–23.
9. An, J.; Xue, X. Life-cycle carbon footprint analysis of magnesia products. *Resour. Conserv. Recycl.* **2017**, *119*, 4–11. [[CrossRef](#)]
10. Luong, V.-T.; Amal, R.; Scott, J.A.; Ehrenberger, S.; Tran, T. A comparison of carbon footprints of magnesium oxide and magnesium hydroxide produced from conventional processes. *J. Clean. Prod.* **2018**, *202*, 1035–1044. [[CrossRef](#)]
11. Meldrum, F.C. Calcium carbonate in biomineralisation and biomimetic chemistry. *Int. Mater. Rev.* **2003**, *48*, 187–224. [[CrossRef](#)]
12. De Silva, P.; Bucea, L.; Moorehead, D.R.; Sirivivatnanon, V. Carbonate binders: Reaction kinetics, strength and microstructure. *Cem. Concr. Compos.* **2006**, *28*, 613–620. [[CrossRef](#)]
13. Van Mechelen, D.; Quaghebeur, M.; Nielsen, P. Method for Producing a Bonded Article Comprising a Press-Moulded, Carbonated Granular Material. EP2771305B1, 2 October 2019.
14. Quaghebeur, M.; Nielsen, P.; Horckmans, L.; Van Mechelen, D. Accelerated Carbonation of Steel Slag Compacts: Development of High-Strength Construction Materials. *Front. Energy Res.* **2015**, *3*, 52. [[CrossRef](#)]
15. Konlechner, D.; Kappacher, G. Achieving the Carbon-Neutral Production of Magnesia and Silica Products Using a HCl-Based Process in Serpentine Feedstock. *Mater. Proc.* **2021**, *5*, 19.

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