

Article

Synthesis of Magnesium Carbonate via Carbonation under High Pressure in an Autoclave

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Abstract: Magnesium carbonate powders are essential in the manufacture of basic refractories capable of withstanding extremely high temperatures and for special types of cement and powders used in the paper, rubber, and pharmaceutical industries. A novel synthesis route is based on CO₂ absorption/sequestration by minerals. This combines the global challenge of climate change with materials development. Carbon dioxide has the fourth highest composition in earth's atmosphere next to nitrogen, oxygen and argon and plays a big role in global warming due to the greenhouse effect. Because of the significant increase of CO₂ emissions, mineral carbonation is a promising process in which carbon oxide reacts with materials with high metal oxide composition to form chemically stable and insoluble metal carbonate. The formed carbonate has long-term stability and does not influence the earth's atmosphere. Therefore, it is a feasible and safe method to bind carbon dioxide in carbonate compounds such as magnesite. The subject of this work is the carbonation of an olivine (Mg₂SiO₄) and synthetic magnesia sample (>97 wt% MgO) under high pressure and temperature in an autoclave. Early experiments have studied the influence of some additives such as sodium bicarbonate, oxalic acid and ascorbic acid, solid/liquid ratio, and particle size on the carbonation efficiency. The obtained results for carbonation of olivine have confirmed the formation of magnesium carbonate in the presence of additives and complete carbonation of the MgO sample in the absence of additives.

Keywords: MgCO₃-powder; synthesis; CO₂-absorption; olivine carbonation; autoclave; thermal decomposition; CO₂ utilization

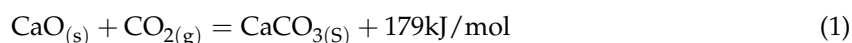
1. Introduction

The significance of the results coming from greenhouse gas (GHG) emissions to both the atmosphere and our lives has already been urged and is nowadays well-known. Because of the continuous increase of CO₂ concentration in the atmosphere since the industrial revolution, various

techniques are proposed. Carbon capture and utilization (CCU) is considered as the most promising technique in order to use the product in cement, transforming it into insoluble carbonate (mainly calcite and magnesite), that is able to remain stable in a geological timeframe [1].

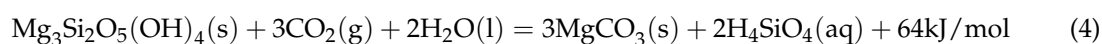
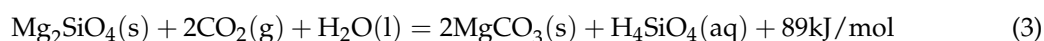
In order to accelerate mineral carbonation, some pretreatment processes are required (microwave heating, grinding, sieving, separation, thermal decomposition, and chemical treatment). The main goal of pre-treatment processes is to increase the carbonation rate and improve the process kinetics. Typical pre-treatment methods are particle size reduction, magnetic separation and thermal treatment. Particle size reduction incorporates various grinding methods for an increase of specific surface area. In magnetic separation, undesired ferrous particles are separated from the rest of the feedstock. Thermal treatment is necessary for hydrated minerals, such as serpentine that contains H₂O molecules in the mineral structure. Pre-treatment is usually required in direct carbonation processes [2]. However, one must consider the balance between increase of reaction rate and additional energy costs, possible CO₂-production related to energy supply and the influence on the beneficial utilization of the final products. The major problem of pre-treatment is its high energy input, i.e., thermal treatment should be avoided due to the high energy demand and CO₂-emissions (depending on the energy source). Overall, the most potentially economical pre-treatment proved to be size reduction [3]. Although there are large resources, it is not a feasible feedstock material because of its crystallographic stability and thus the necessary step of thermal pre-treatment.

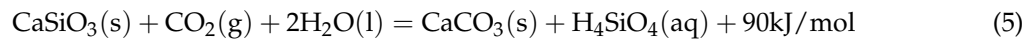
Industrially produced by-products containing alkaline metals are also feasible for mineral carbonation, such as numerous types of slags, scraps, red gypsum, combustion residues, fly ashes and other forms of metal oxide materials such as red mud [4]. Unlike natural feasible materials, industrial by-products usually do not require mining and pretreatment processes for utilization because they already have high alkaline metal contents which are sufficient for mineral carbonation [5]. Because of high availability in minerals and secondary materials among all of the possible materials selections, calcium oxide and magnesium oxide are the most favorable options, as shown in Equations (1) and (2) [6,7].



Although the carbonation process is an exothermic reaction, it requires an additional heat for better dissolution of carbon dioxide in water in order to form magnesium carbonate. The benefits of exothermic mineral carbonation may result in a positive net energy balance, which improves the net efficiency of a combined cycle power plant [8]. Calculating energy balances of the process is essential for the determination of the process' profitability which might be influenced by high energy costs. Furthermore, the overall reduction of carbon dioxide emissions has to be considered due to further emissions in the mineral carbonation process resulting from, e.g., transportation, grinding and processing of by-products. Furthermore, the potential use of the formed products should also be taken into consideration.

There are abundant calcium and magnesium rich minerals available in the earth's crust. Although MgO and CaO are the most abundant alkali and alkaline metal oxides, they cannot be found as binary oxides in nature. Usually, they exist as hydroxides or silicate minerals. In a mineral carbonation process, these can also be used as feedstock to form carbonates that are chemically stable in a geological timeframe. Silicate minerals usually are richer in alkaline metal content such as magnesium, sodium, and calcium. Common silicate minerals suitable for carbonation are forsterite (Mg₂SiO₄), antigorite (Mg₃Si₂O₅(OH)₄) and wollastonite (CaSiO₃) and their overall reaction conversions are given in Equations (3) to (5).





The aforementioned mineral carbonation using slags as reactant also have the chance to be profitable if they are built closely to the steel production site in order to reduce production costs [9]. Furthermore, heat integration with the steel production plant can reduce overall energy costs significantly [9]. Carbonation of different types of slags are widely studied, one study by Georgakopoulos [4] suggests that blended hydraulic cement BHC slag has the highest conversion rate which is 68.3%.

Red gypsum usually exists in the form of calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Typically, red gypsum has a purity of 95% and has large resources in Malaysia [10]. Due to the large calcium content its carbonation is also a promising CCS option, i.e., one ton of red gypsum can stably bind 0.26 tons of gaseous CO_2 . A big advantage of red gypsum as carbonation resource is no mining cost is required since it exists in the form of fine powder which favors the carbonation reaction.

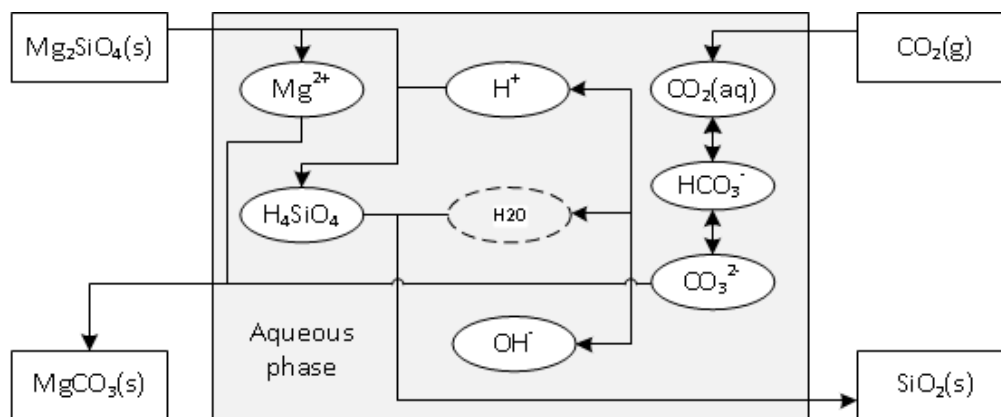
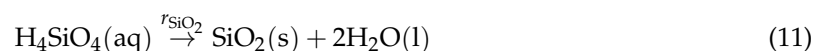
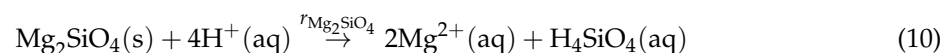
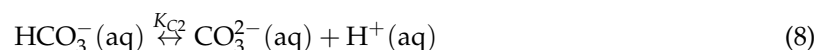
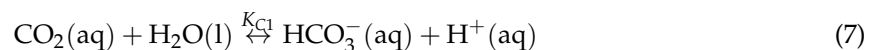


Figure 1. Reaction path of direct forsterite carbonation in aqueous solution.

Generally, the reaction path for the indirect carbonation of forsterite in an aqueous solution can be described by Equations (6) to (12) which is also illustrated in Figure 1 [11,12]. For simplicity, olivine consists only of Mg_2SiO_4 , namely forsterite. First, gaseous carbon dioxide dissolves in the aqueous solution at a certain mass transfer rate as in Equation (6). Simultaneously, forsterite is dissolved in the aqueous solution (Equation (10)). In the aqueous solution, all species are assumed to be at equilibrium: Aqueous CO_2 dissociates into bicarbonate, which further dissociates into carbonate (Equations (7) and (8)). Self-ionization of water is given by Equation (9). Aqueous silicic acid then precipitates as amorphous silica, which is a by-product, and lastly magnesium ions and carbonate form magnesite (Equations (11) and (12)).



The particular process is characterized by several equilibrium and non-equilibrium reactions. The determination of process parameters such as temperature, pressure and pH for maximum overall

conversion rates is elementary. Direct CO₂ sequestration at high pressure with olivine as a feedstock has already been performed in numerous studies at different temperatures and pressures with or without the use of additives such as carboxylic acid, and sodium hydroxide [11,12]. It is reported that optimal reaction conditions are in the temperature range of 150–185 °C and in the pressure range of 135–150 bar [10]. Additives are reported to have a positive influence on carbonation rate. Optimal addition of additives are reported by Bearat et al. [13] in studies about the mechanism that limits aqueous olivine carbonation reactivity under the optimum sequestration reaction conditions observed as follows: 1 M NaCl + 0.64 M NaHCO₃, at 185 °C and P (CO₂) about 135 bar. A reaction limiting silica-rich passivating layer forms on the feedstocks grains, slowing down carbonate formation and raising process costs. Eikeland [14] reported that NaCl does not have significant influence on carbonation conversion. The presented results show a conversion rate of more than 90% using a NaHCO₃ concentration of 0.5 M, without adding of NaCl. Ideally, the solid phases exist as pure phases without growing together. In reality, different observations are made on the behavior of solid phases. Daval et al. [15] reported about high influence of amorphous silica layer formation on the dissolution rate of olivine at 90 °C and elevated pressure of carbon dioxide. This passivating layer may either built up from non-stoichiometric dissolution, precipitation of amorphous silica on forsterite particles or a combination of both. In contrast to that, Oelkers et al. [16] and Hänchen [17] observed stoichiometric dissolution and no build-up of a passivating layer except during start-up of experiments. Additionally, magnesite may precipitate on undissolved forsterite particles leading to a surface area reduction and therefore a reduction on forsterite dissolution rate, which was reported by Turri et al. [18]. Besides this undesired intermixing of solids, they observed pure particles of magnesite to be predominant in the smallest particle class, amorphous silica particles to be mainly present in the intermediate particle class and unreacted olivine particles to be predominant in the largest particle class. This knowledge may be of value for subsequent separation of products.

CO₂ sequestration with olivine as a feedstock was performed in a rocking batch autoclave at 175 °C and 100 bars in an aqueous solution and a CO₂-rich gas phase from 0.5 to 12 h. Turri showed maintainable recovery of separate fractions of silica, carbonates and unreacted olivine. Characterization of the recovered solids revealed that carbonates predominate in particle size range below 40 µm. The larger, residue fraction of final product after carbonation consisted mainly of unreacted olivine, while silica is more present in the form of very fine particles. An addition of sodium hydrogen carbonate at 0.64 M, oxalic acid at 0.5 M and ascorbic acid at 0.01 M was successfully applied in order to obtain maximal carbonation. The positive influence of the above-mentioned additives on the carbonation efficiency was reported by Olajire [19]. They studied the technology of CO₂ sequestration by mineral carbonation with current status and future prospects, but the positive influence of additives was not explained in detail.

Formation of submicron magnesite during reaction of natural forsterite in H₂O-saturated supercritical CO₂ was studied between 35 and 80 °C and at pressure of 90 bars [20]. The magnesite particles formed under below-mentioned conditions exhibited an extremely uniform submicron grain-size and nearly identical rhombohedral morphologies at all temperatures. Then an evidence for carbonate surface complexation during forsterite carbonation in wet supercritical carbon dioxide was also considered. The effect of Fe on the measured rates of olivine carbonation and its role in the formation of Si-rich surface layers, which can significantly inhibit olivine dissolution and limit the extent of the carbonation reaction was considered by Saldi et al. [21]. A series of batch and flow-through reactor experiments was conducted in pure water at 90 and 150 °C and under a CO₂ partial pressure of 100 and 200 bar, using both a natural sample of Fe-bearing olivine and a synthetic sample of pure forsterite. Experimental results show that Fe plays an ambivalent role in the carbonation.

The preparation of a magnesium hydroxy carbonate from magnesium hydroxide and carbon dioxide includes the formation of a magnesium hydroxide slurry and sparging CO₂ gas through it. Various experimental conditions are evaluated in order to obtain the conditions that result in the formation of the magnesium hydroxy carbonate [22].

Our paper deals with the formation of magnesium carbonate using an Italian olivine (35.57 wt% MgO) and a synthetic reference material, mainly consisting of magnesia (97.56 wt% MgO) with special attention on the influence of the additives and different solid/liquid ratio. After carbonation, the settled solid fraction contained mainly carbonation products, which was studied by structure and composition analysis (X-Ray Diffraction XRD) and reactivity (Thermogravimetric analysis TGA and Differential Scanning Calorimetry DSC). The water solution was analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy ICP-OES in order to determine the concentration of nickel, iron, magnesium and cobalt.

2. Experimental Section

The samples used were Italian olivine (Figure 2a) and a high-grade synthetic dead burned magnesia (Figure 2b). From its chemical composition apart from the chromite present at approx. 0.45 wt% and other inert minerals at trace levels, the olivine was considered as a mixed Mg-Ni and Fe silicate.

The olivine has been delivered with a particle size of below 200 μm , the used magnesia has a grain size between 10 and 30 mm. Particle Size Distribution PSD Analysis was performed used Mastersizer Hydro 2000G (Malvern PANalytical GmbH, Kassel, Germany)

The carbonation tests were planned for the three different particle size fractions <20 μm , 20–63 μm and 100–200 μm in order to evaluate the optimal process parameters and the use of additives.

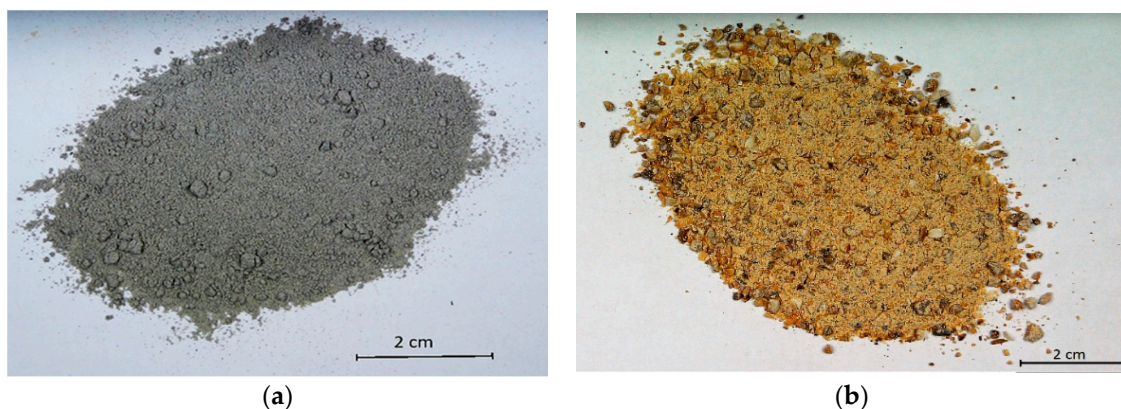


Figure 2. (a) Photos of Italian Olivine; (b) Reference material after grinding.

The olivine with $d_{90} = 100 \mu\text{m}$ (90% below 100 microns) as it is presented in the sieve analysis in Figure 3 has been sieved wet to produce the three grain size fractions. The magnesia sample has been crushed and milled in a lab-scale jaw crusher and has also been sieved wet into the required grain size fractions.

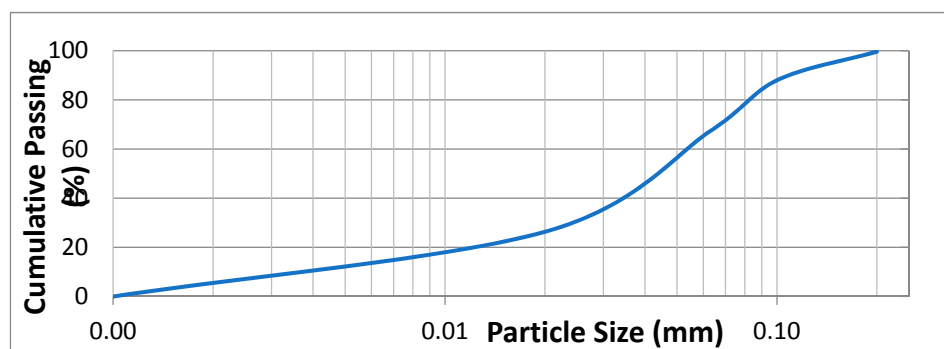


Figure 3. Sieve Analysis (Particle Size Distribution PSD) of olivine <200 μm .

The chemical composition of olivine and magnesia was analyzed by X-ray fluorescence XRF using Device PW2404 (Malvern Panalytical B.V., Eindhoven, Netherlands), such is presented in Table 1.

Table 1. Chemical composition of the investigated olivine and magnesia in wt%.

Components	Olivine	Magnesia
SiO ₂	46.43	0.32
Al ₂ O ₃	2.55	0.20
Fe ₂ O ₃	10.88	0.58
TiO ₂	0.11	0.05
CaO	2.16	0.75
MgO	35.57	97.56
K ₂ O	0.39	0.02
Na ₂ O	0.17	0.10
MnO	0.17	0.24
Cr ₂ O ₃	0.45	0.00
P ₂ O ₅	0.00	0.00
ZrO ₂	0.02	0.03
SO ₃	0.00	0.00
BaO	0.00	0.00
ZnO	0.08	0.08
NiO	0.89	0.09
Co ₃ O ₄	0.08	0.00
CuO	0.06	0.00
Total	100.00	100.00

The planned experiments are shown in Table 2.

Table 2. Experimental plan (T = 175 °C, pCO₂: 117 bar, 300 rpm, 4 h).

Exp. No	S/L (g/mL H ₂ O)	Fraction Size (μm)	Concentration of Additives in Water, (mol/L)	Material
1	10/150 (0.066)	100–200	No	Olivine, Italy (35.57 wt% MgO)
2	10/150 (0.066)	<20	No	Olivine, Italy (35.57 wt% MgO)
3	30/150 (0.2)	20–63	0.64 NaHCO ₃ 0.06 H ₂ C ₂ O ₄ 0.003 C ₆ H ₈ O ₆ ,	Olivine, Italy (35.57 wt% MgO)
4	30/150 (0.2)	20–63	No	Synthetic magnesia (97.56 wt% MgO)

Carbonation tests have been carried out in the 250 mL autoclave from Parr Instrument Company (Moline, IL, USA), USA as shown in Figure 4 at 175 °C and 117 bars with pure grade CO₂. An amount ranging from 10 to 30 g olivine has been added to 150 mL solution in different experiments.

After reaction, the liquid had very low contents of metal cations, therefore characterization of the reaction products was restricted to the solid phase by TGA/DSC using Instrument STA 449F3 with Proteus Software (NETZSCH, Selb, Germany) and XRD-Analysis using Bruker D8 Advance with LynxEye detector (Bruker AXS, Karlsruhe, Germany). X-ray powder diffraction patterns were collected on a Bruker-AXS D4 Endeavor diffractometer in Bragg–Brentano geometry, equipped with a copper tube and a primary nickel filter providing Cu $K\alpha_{1,2}$ radiation ($\lambda = 1.54187 \text{ \AA}$).



Figure 4. Parr Autoclave with maximum pressure of 200 bar and maximum temperature of 250 °C.

3. Results and Discussion

The characterization of products was performed using TGA, DSC, XRD and ICP-OES analysis (SPECTRO ARCOS, SPECTRO Analytical Instruments GmbH, Kleve, Germany) in order to confirm the formation of MgCO_3 . Additionally, the influence of additives on carbonation was discussed.

3.1. Product Characterization—XRD Analysis of Product after Carbonation

To evaluate the overall capability of the carbonation process, an experiment was performed on a synthetic reference material (>97 wt% MgO) considering the present mineralogical phases detected via XRD before and after the carbonation (Figures 5 and 6).

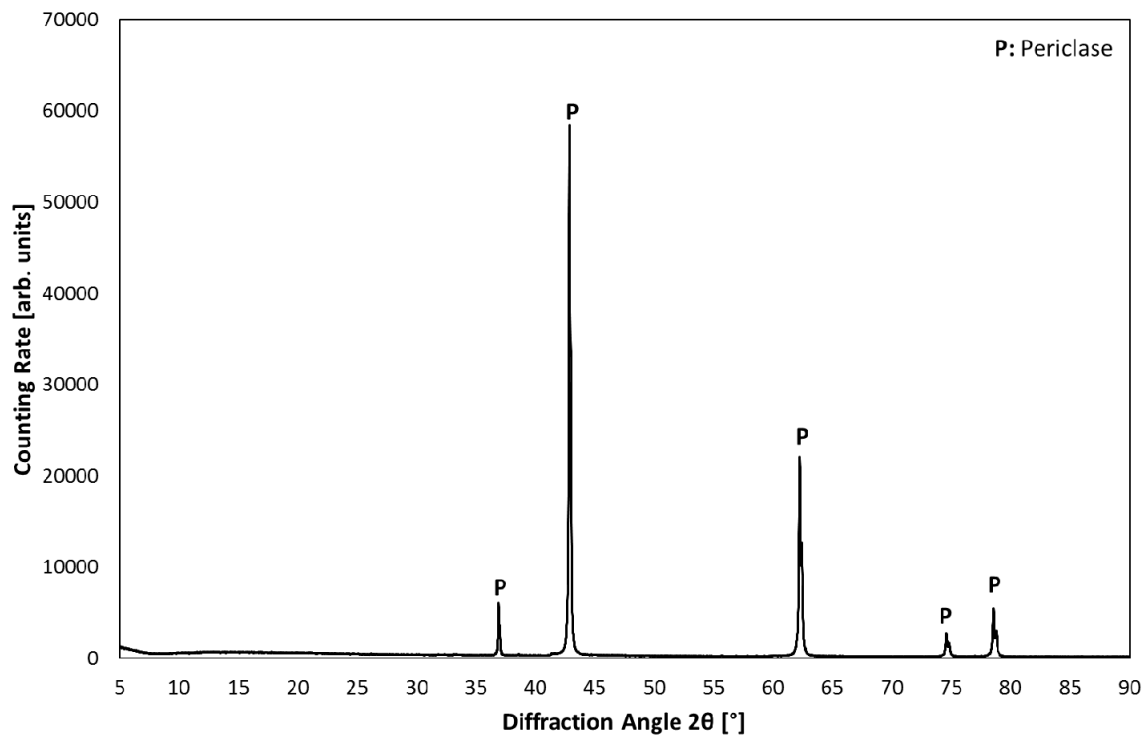


Figure 5. XRD analysis of reference material.

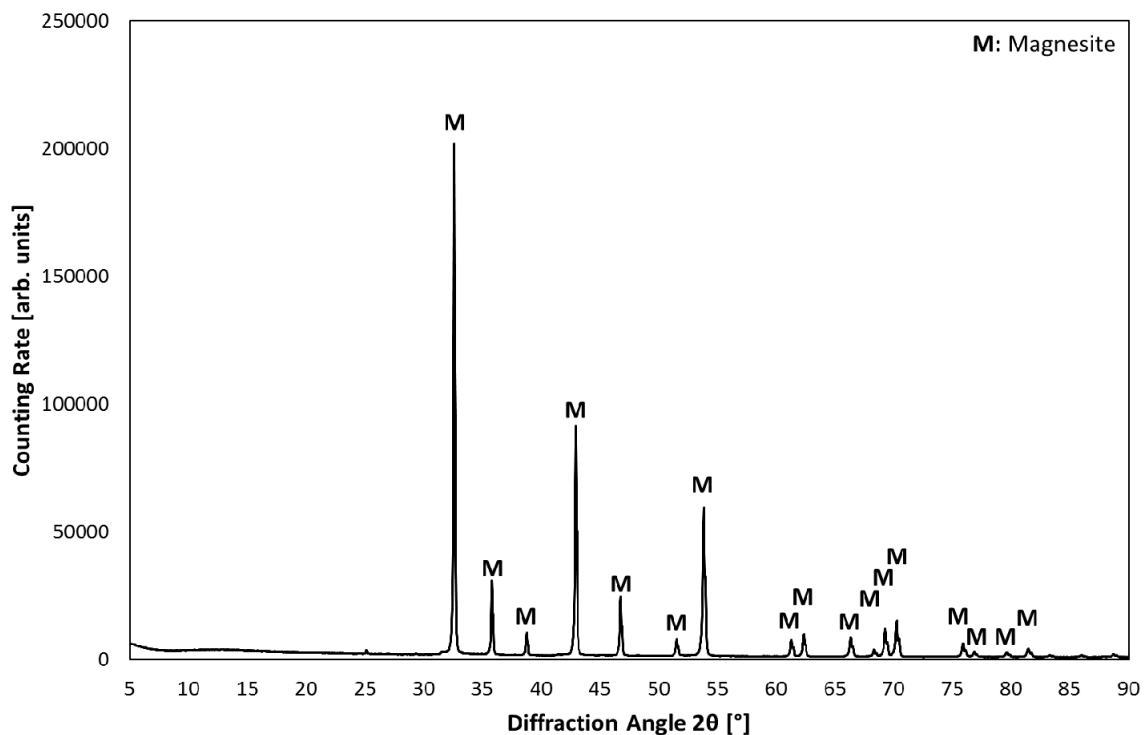


Figure 6. XRD analysis of reference sample after carbonation process.

The results prove the formation of magnesite (MgCO_3) out of periclase (MgO) in the absence of any additives. Both XRD patterns show the existence of a single phase, which underlines the capability of both the reference material and the carbonation process. In the next step of the present study, the carbonation process was applied to an Italian olivine sample as an exemplary natural raw material aiming at a comparable MgCO_3 formation as observed utilizing a synthetic reference material. XRD analysis of the initial olivine sample confirms the presence of forsterite, enstatite, clinoenstatite,

lizardite, spinel and tremolite, based on hydroxide and silicate of magnesium, calcium and iron (Figure 7).

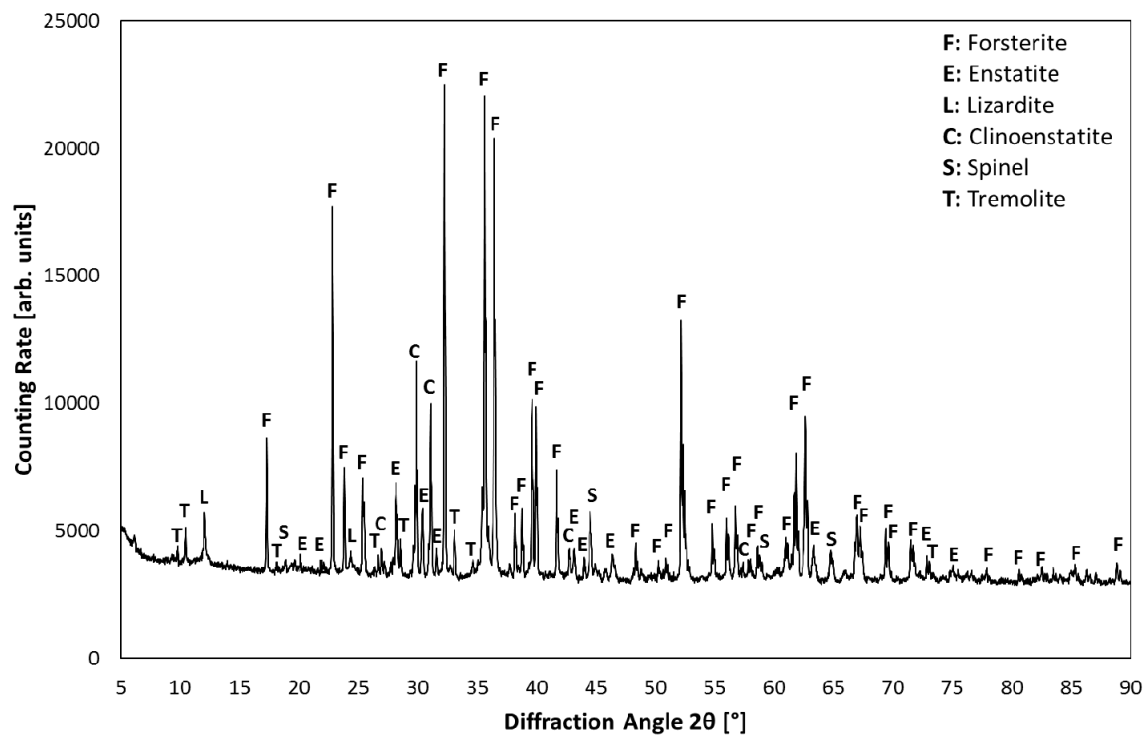


Figure 7. XRD analysis of initial olivine sample.

Unfortunately, the chosen parameters (investigated fraction of 100–200 μm , solid/liquid ratio of 0.066 at 175 $^{\circ}\text{C}$ and 117 bar) did not contribute to the formation of magnesite as analyzed by XRD. Applying the same experimental conditions on an olivine sample ground to a particle size below 20 μm did not yield any magnesite formation as well. However, followed by the addition of NaHCO_3 , $\text{H}_2\text{C}_2\text{O}_4$ and $\text{C}_6\text{H}_8\text{O}_6$ the formation of MgCO_3 can be proved via XRD (Figure 8) when using a fraction size of 20–63 μm .

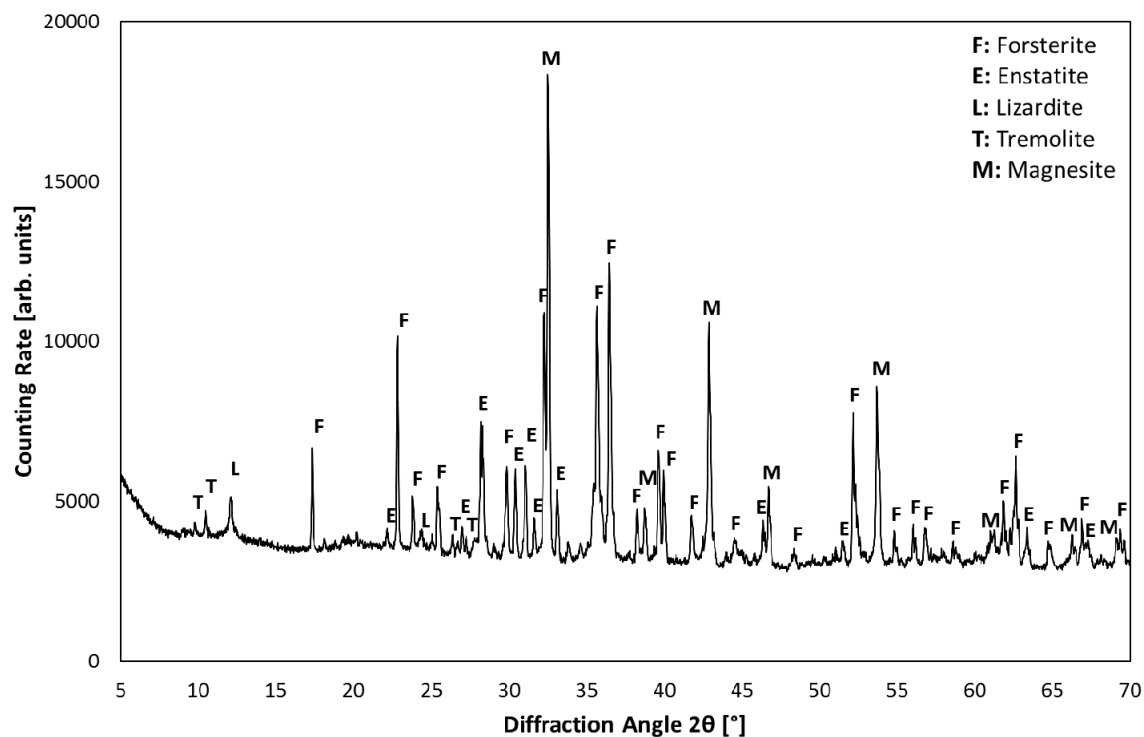


Figure 8. XRD analysis of olivine sample after carbonation.

3.2. Analysis of Water Solution after Carbonation of an Olivine

The ICP-OES analysis of water solution after carbonation, as shown in Table 3 confirms very small dissolution of valuable elements such as cobalt. The most dominant species are magnesium and silicon in the order of magnitude of mg/L what corresponds to few percent of leaching efficiency. The pH value confirmed that the solution is a neutral medium.

Table 3. Chemical analysis of Si, Mg, Fe, Ni, Cr, and Al in solution (mg/L) after carbonation.

Exp. No.	Si	Mg	Fe	Ni	Cr	Co	Al
2 (pH-6.7)	166	229	0.11	0.73	<1	<1	<1
3 (pH-7.3)	195	705	67	10	<1	<1	<1
4 (pH-2.32)	<1	211	<1	<1	<1	<1	<1

3.3. Carbonation Extent

Thermogravimetric analysis measurements were performed in order to establish the carbonation effect. The calculated carbonation was about 45% in the presence of additives, as shown in Figure 9.

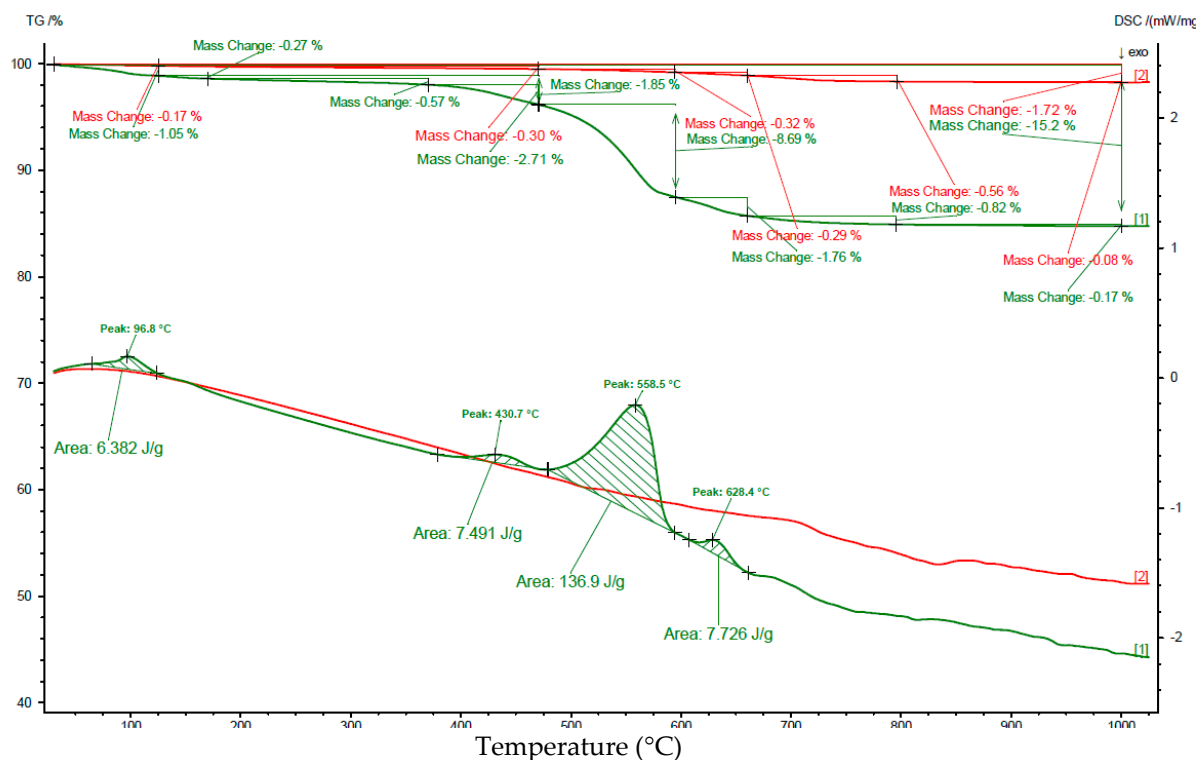


Figure 9. TGA/DSC Analysis in Exp. 3 in the presence of additives.

The total analysis of thermal decomposition of formed $(\text{Mg,Fe})\text{CO}_3$ is shown in Table 4.

Table 4. Thermal Decomposition of samples before carbonation and after carbonation.

Interval	Before Carbonation		After Carbonation		
	Interval [°C]	Loss of weight [%]	Peak area [J/g]	Loss of weight [%]	Peak area [J/g]
25–125	25–125	0.17		1.05	6.38
125–385	125–385	0.22		0.93	No peak
385–470	385–470	0.08	no peak	1.77	8.36
470–595	470–595	0.32		8.69	137
595–660	595–660	0.29		0.75	7.73
660–725	660–725	0.44	4.40	0.62	4.10
725–1000	725–1000	0.20	No peak	0.36	No peak
25–1000	25–1000	1.7		15.2	

As shown in Table 4, the total weight loss for an initial sample of the Italian olivine in the interval between 25 and 1000 °C amounts 1.7%, what is the amount of bound water in the used sample. The total weight loss for the initial olivine material in the interval between 25 and 470 °C amounts 0.47% in comparison to 3.75% for this sample after carbonation. In difference for the sample without carbonation, in the temperature interval between 470 °C and 595 °C, the weight loss amounts 8.69%, with a thermal effect of 137 J/g, what confirms that this temperature range is most important for thermal decomposition of $(\text{Mg,Fe})\text{CO}_3$. Above 775 °C the change of weight is not significant, and thermal decomposition of sample is minimal, what means that the thermal decomposition is finished. In contrast to this experiment in the presence of additives in Exp. 3 with loss of weight of 15.2%, the overall weight losses of experiment 1 is very small (few percent) what confirms a low carbonation degree (as confirmed with XRD analysis in Figure 6). The weight loss for experiment 2 is about 3.5% (red line at Figure 10) which confirms very small carbonation rate in the absence of additives in comparison to the experiments with additives.

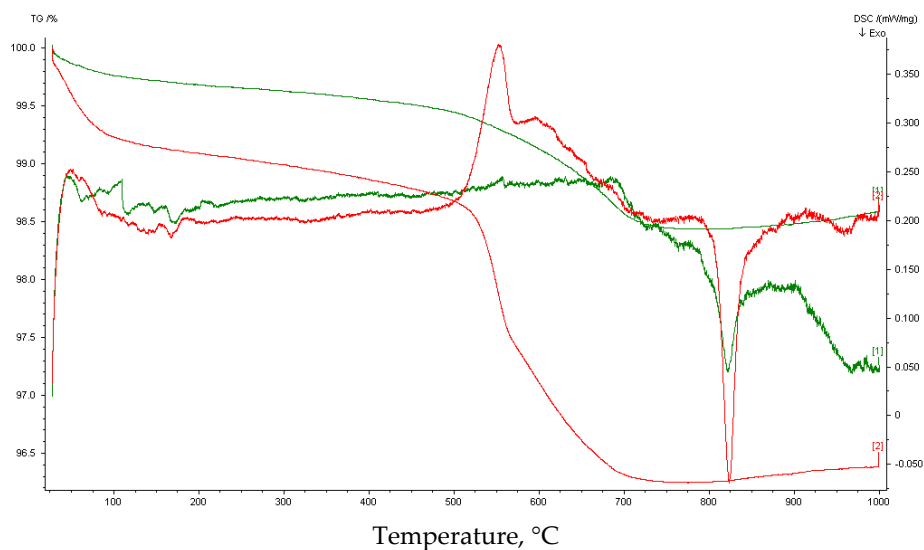
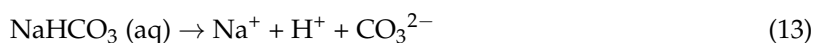
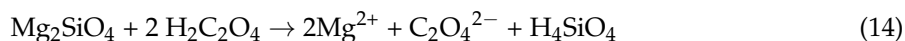


Figure 10. TGA and DSC Analysis in the experiments 1 and 2 (TGA and DSC for experiment 1- green color; TGA and DSC for experiment 2- red color).

This positive effect may be due to “reaction-driven cracking” in the presence of NaHCO₃, formation of etch pits, and/or other processes that continually renew the reactive surface area of Mg₂SiO₄.



An addition of oxalic acid leads to formation of Mg-ions in solution, which react with carbonate ions forming magnesium carbonate.



The two analyses of thermal decomposition of products after carbonation of magnesia (97 wt%) confirmed total decomposition of the produced MgCO₃.

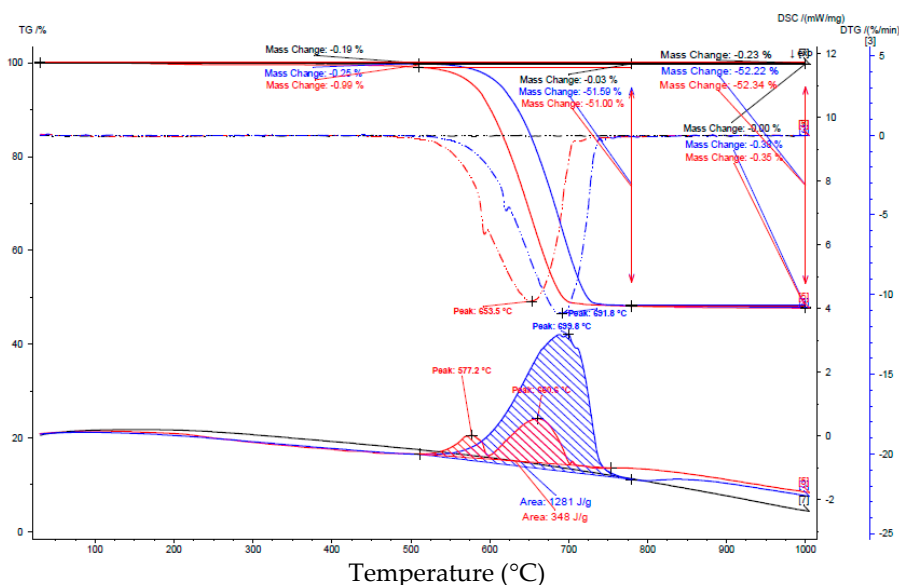


Figure 11. TGA and DSC Analysis of formed product after carbonation of synthetic magnesia (20 °C/min, nitrogen, Exp. 4).

As shown at Figure 11, the weight loss of 52.34 % (TGA-red line) and 52.22 (TGA-blue line) with maximal DSC effect (1281 J/g; blue area) at $T_{\max} = 699.8$ °C confirm the formation of magnesium carbonate, what was compared with theoretical value, according to the Equation (16):



where: $M(\text{Mg}) = 24.30$ g/mol; $M(\text{MgCO}_3) = 84.30$ g/mol, $M(\text{MgO}) = 40.30$ g/mol, $M(\text{CO}_2) = 44.0$ g/mol.

Using a ratio between molar mass of magnesium carbonate and magnesium oxide, theoretical calculated loss of carbon dioxide amounts 52.55%, what is in good accordance with an experimental determined weight loss. Finally, it confirms the completed carbonation of synthetic magnesia under the chosen parameters and formation of magnesium carbonate, which particle size distribution was shown at Figure 12.

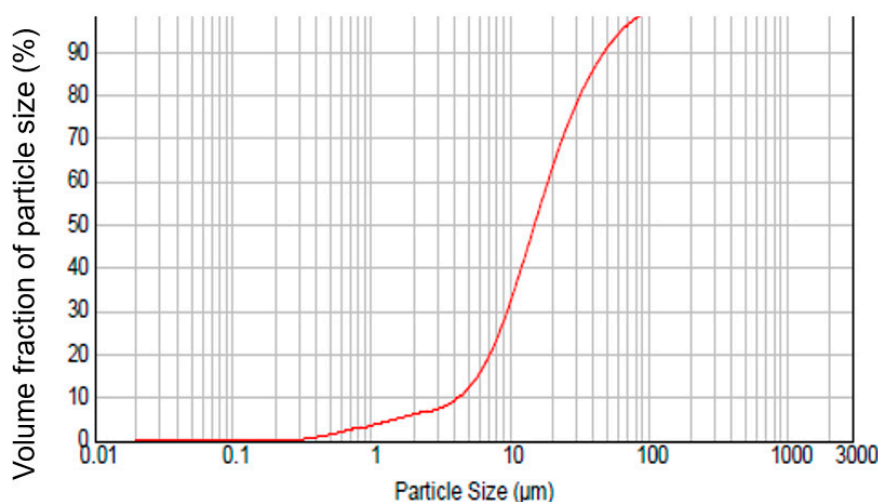


Figure 12. Particle size distribution of MgCO_3 after carbonation of synthetic magnesia.

The measured values of produced magnesium carbonate d_{50} and d_{84} amount 15.066 and 37.066 μm , respectively.

4. Conclusion

Synthesis of magnesium carbonate was studied via carbonation of olivine using different size fractions (under 20 μm , between 20 and 63 μm , and between 100 and 200 μm) with different solid/liquid ratios of 1:15 and 1:5; at 175 °C and pressure of CO_2 (117 bar) in an autoclave in the presence and in the absence of additives. The characterization of products using XRD, TGA, PSD and DSC analysis has confirmed the formation of MgCO_3 . In contrast to carbonation of olivine in the absence of additives the formation of magnesium carbonate is possible at high pressure and temperature with olivine (35.57% MgO) from Italy in the presence of sodium hydrogen carbonate, oxalic acid, and ascorbic acid at 175 °C, 117 bar in 4 h (Exp. 3). The maximum carbonation (more than 95%) was obtained at the same conditions for synthetic magnesia (97.56 wt% MgO) in the absence of additives. In order to validate the first results in 0.25 L autoclave, new scale up experiments will be performed in 1.0 and 10.0 L autoclaves. Especially, the influence of rotating speed, pH-values and different initial secondary materials such as slag and red mud shall be analyzed in our future work. The analysis of the obtained solution after carbonation revealed very small content of cobalt and chromium, but it will be also considered in our future work in the presence of pH buffering agents in order to increase an extraction efficiency. Especially, a life-cycle-assessment of the carbonation process in the presence of additives will be performed in our future work.

Author Contributions: S.S. conceptualized and managed the research, and co-wrote the paper. D.K. performed the preparation of the olivine materials (grinding, sieving) and co-wrote the paper. H.W. co-wrote the paper. S.N. has performed experiments in an autoclave. P.K. has performed of XRD and TGA-analysis of initial sample and obtained products. G.M. helped in discussion of TGA and XRD-analysis. C.D. analyzed the data and co-wrote the paper. S.E. supervised the XRF- and XRD-analyses and co-wrote the paper with R.T., P.K. conceptualized the research and provided industrial advice. D.R. managed the laboratory facilities for TGA and DSC analysis in Heidelberg Cement Technology Center. B.F. supervised the personnel, provided funding and co-wrote the paper.

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References

1. Nduagu, E.; Björklöf, T.; Fagerlund, J.; Mäkilä, E.; Salonen, J.; Geerlings, H.; Zevenhoven, R. Production of magnesium hydroxide from magnesium silicate for the purpose of CO₂ mineralization—Part 2: Mg extraction modeling and application to different Mg silicate rocks. *Miner. Eng.* **2012**, *30*, 87–94. [[CrossRef](#)]
2. Huijgen, W.J.J.; Comans, R.N.J. *Carbon Dioxide Sequestration by Mineral Carbonation. Literature Review 2003–2004*; Technol Report; Energy Research Centre of the Netherlands: Petten, The Netherlands, December 2005.
3. Santos, R.; Verbeeck, W.; Knops, P.; Rijnsburger, K.; Pontikes, Y.; Gerven, T. Integrated mineral carbonation reactor technology for sustainable carbon dioxide sequestration: “CO₂ Energy Reactor”. *Energy Procedia* **2013**, *37*, 5884–5891. [[CrossRef](#)]
4. Georgakopoulos, E.D. Iron and steel slag valorization through carbonation and supplementary processes. Ph.D. Thesis, Cranfield University, Cranfield, UK, December 2016.
5. Santos, R.; Audenaerde, A.; Chiang, Y.; Iacobescu, R.; Knops, P.; Gerven, T. Nickel Extraction from olivine: Effect of carbonation pretreatment. *Metals* **2015**, *5*, 1620–1644. [[CrossRef](#)]
6. Chang, E.; Pan, S.; Chen, Y.; Tan, C.; Chiang, P. Accelerated carbonation of steelmaking slags in a high-gravity rotating packed bed. *J. Hazard. Mater.* **2012**, *227*, 97–106. [[CrossRef](#)]
7. Aminu, M.; Nabavi, S.; Rochelle, C.; Manovic, V. A review of developments in carbon dioxide storage. *Appl. Energy* **2017**, *208*, 1389–1419. [[CrossRef](#)]
8. Azdarpour, A.; Asadullah, M.; Mohammadian, E.; Hamidi, H.; Junin, R.; Karaei, M. A review on carbon dioxide mineral carbonation through pH-swing process. *Chem. Eng. J.* **2015**, *279*, 615–630. [[CrossRef](#)]
9. Chang, E.; Pan, S.; Chen, Y.; Chu, H.; Wang, C.; Chiang, P. CO₂ sequestration by carbonation of steelmaking slags in an autoclave reactor. *J. Hazard. Mater.* **2011**, *195*, 107–114. [[CrossRef](#)] [[PubMed](#)]
10. Rahmani, O.; Junin, R.; Tyrer, M.; Mohsin, R. Mineral carbonation of red gypsum for CO₂ sequestration. *Energy Fuels* **2014**, *28*, 5953–5958. [[CrossRef](#)]
11. Bremen, A.M.; Mhamdi, A.; Mitsos, A. Mineral carbonation modeling and investigation on relevant parameters. In Proceedings of the Internal Project Meeting, Aachen, Germany, 13 November 2017.
12. Bremen, A.M.; Mhamdi, A.; Mitsos, A. Mineral carbonation model status update. In Proceedings of the Internal Project Meeting, Aachen, Germany, 7 September 2018.
13. Béarat, H.; McKelvy, M.; Chizmeshya, A.; Gormley, D.; Nunez, R.; Carpenter, R.; Squires, K.; Wolf, G. Carbon sequestration via aqueous olivine mineral carbonation: Role of Passivating layer formation. *Environ. Sci. Technol.* **2006**, *40*, 4802–4808. [[CrossRef](#)] [[PubMed](#)]
14. Eikeland, E.; Bank, A.; Tyrsted, C.; Jensen, A.; Iversen, B. Optimized carbonation of magnesium silicate mineral for CO₂ storage. *Appl. Mater. Interfaces* **2015**, *7*, 5258–5264. [[CrossRef](#)] [[PubMed](#)]
15. Daval, D.; Sissmann, O.; Menguy, N.; Salsi, G.; Gyot, F.; Martinez, I.; Corvisier, J.; Machouk, I.; Knauss, K.; Hellmann, R. Influence of amorphous silica layer formation on the dissolution rate of olivine at 90 °C and elevated pCO₂. *Chem. Geol.* **2011**, *284*, 193–209. [[CrossRef](#)]
16. Oelkers, E. An experimental study of forsterite dissolution rates as a function of temperature and aqueous Mg and Si concentrations. *Chem. Geol.* **2001**, *175*, 485–494. [[CrossRef](#)]
17. Hänchen, M.; Prigiobbe, V.; Storti, G.; Seward, T.M.; Mazzotti, M. Dissolution kinetics of forsteritic olivine at 90–150 °C including effect of the presence of CO₂. *Geochim. Cosmochim. Acta* **2006**, *70*, 4403–4416. [[CrossRef](#)]

18. Turri, L.; Muhr, H.; Rijnsburger, K.; Knops, P.; Lopicque, F. CO₂ sequestration by high pressure reaction with olivine in a rocking batch autoclave. *Chem. Eng. Sci.* **2017**, *171*, 27–31. [[CrossRef](#)]
19. Olajire, A. A review of mineral carbonation technology in sequestration of CO₂. *J. Pet. Sci. Eng.* **2013**, *109*, 364–392. [[CrossRef](#)]
20. Qafoku, O.; Hu, J.; Hess, N.; Hu, M.; Ilton, E.; Feng, J.; Arey, B.; Felmy, A. Formation of submicron magnesite during reaction of natural forsterite in H₂O-saturated supercritical CO₂. *Geochim. Cosmochim. Acta* **2014**, *134*, 197–209. [[CrossRef](#)]
21. Saldi, G.; Daval, D.; Morvan, G.; Knauss, K. The role of Fe and redox conditions in olivine carbonation rates: An experimental study of the rate limiting reactions at 90 and 150 °C in open and closed systems. *Geochim. Cosmochim. Acta* **2013**, *118*, 157–183. [[CrossRef](#)]
22. Botha, A.; Strydom, C. Preparation of a magnesium hydroxy carbonate from magnesium hydroxide. *Hydrometallurgy* **2001**, *62*, 175–183. [[CrossRef](#)]



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