



High pressure carbonation of olivine

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Abstract

Because of the significant increase of CO₂ emissions, mineral carbonation is a promising process in which carbon dioxide reacts with materials containing high metal oxide composition such as magnesium oxide, calcium oxide and iron oxide to form metal carbonate. The formed carbonate has long-term stability and does not influence the earth's atmosphere. The subject of this work is the carbonation of an olivine (Mg₂SiO₄) from Norway and reference magnesite material under high pressure and temperature in an autoclave. First experiments have confirmed the positive influence of additives such as sodium bicarbonate, oxalic acid and ascorbic acid on the carbonation efficiency. The maximal carbonation efficiency was amounted 79.86 % for NedMag99 reference sample in an autoclave (T = 175 °C, 1 L, 117 bar CO₂, 600 rpm, 2 hours) in the presence of additives of sodium carbonate, oxalic and ascorbic acid. Under same conditions the carbonation efficiency of the Steinsvik olivine was 44.56 %.

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. Most dominantly carbon capture and utilization (CCU) are considered as a 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 a mineral carbonation process, some pre-treatment processes are required (microwave heating, grinding, sieving, separation, thermal decomposition, 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 of, it is not a feasible feedstock material because of its crystallographic stability and thus the necessary step of thermal pre-treatment.

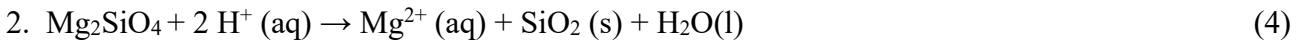
Industrially produced by-products containing alkaline earth metals are also feasible for mineral carbonation, such as numerous types of slags, scraps, red gypsum, combustion residues, fly ashes and other forms of metal oxide waste materials such as red mud [4]. Unlike natural feasible materials, industrial by-products usually do not require mining and pre-treatment processes for utilization because they already have high alkaline earth metal oxide contents which are sufficient for a material carbonation [5]. The large generation of slags during iron and steel production is an economical problem because of their limitation of commercial use, large landfill fees and high environmental risks. The disposal of slags is a growing concern for the industry. Production of slags generates the highest carbon dioxide emission compared to other industrial by-products mainly because of its energy intensive nature and using coal burning as primary fuel for iron and steel production. Slags generated in steel production are 10 – 15 wt.-% of produced steel [6]. The carbonation using slags as reactant could be more energy saving because the carbonation plants usually build close to iron and steel production plants. The transportation cost is lower. And mineral carbonation could reuse heat supply from steel production in order to reduce heating cost.

Among all of the possible materials selections, calcium oxide and magnesium oxide are the most favorable options, as shown in equations 1) and 2) [7]. Because of its high availability in minerals and waste materials and an exothermic reaction during carbonation, calcium oxide and magnesium oxide are the most suitable materials for carbon dioxide sequestration [7].



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 hours. Turri [8] 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.

Stopic et al. [9] have studied the positive influence of the additives during the carbonation of the olivine from Italy (20 – 63 µm) in 250 ml Parr autoclave at 175 °C using 117 bar CO₂ in 4 hours. The mechanism of carbonation contains three most important steps: 1. Dissolution of carbon dioxide in water; 2. Transfer of magnesium from solid mineral to an aqueous phase and 3. Formation of magnesium carbonate [10]:



Regarding to the prospects for application of Carbon Capture and Storage CCS, it was under extensive research and development globally. In Finland, CCS has been a part of the discussions regarding mitigation of climatic change since the nineties, but has been considered expensive and not mature enough in comparison to other measures for reducing CO₂-emissions. The unfavorable conditions in Finland for geological storage of CO₂ have been another reason for the low interest towards CCS [11].

Our paper deals with the formation of magnesium carbonate using the Steinsvik olivine from Norway (41.31 wt.-% MgO), and a reference material, mainly consisting of magnesia (97.56 wt.-% MgO) with special attention on the influence of the additives. After carbonation, the settled solid fraction contained mainly carbonation products, which was determined by structure and composition analysis (XRD) and reactivity (thermal decomposition of a product in a muffle furnace) in order to calculate carbonation efficiency.

2 Experimental

2.1 Material

The used samples used represent olivine from Norway (Steinsvik) and a high-grade synthetic dead burned magnesia (NedMag99) as shown in Table 1:

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

Components	Olivine	Magnesia
SiO ₂	48.46	0.32
Al ₂ O ₃	0.48	0.20
Fe ₂ O ₃	7.77	0.58
TiO ₂	0.02	0.05
CaO	0.12	0.75
MgO	41.31	97.56
K ₂ O	0.10	0.02
MnO	0.12	0.24
Cr ₂ O ₃	0.38	0.00
ZrO ₂	0.01	0.03
ZnO	0.03	0.08
NiO	1.20	0.09



2.2 Procedure

The carbonation of olivine was performed using the operations shown at Figure 1.

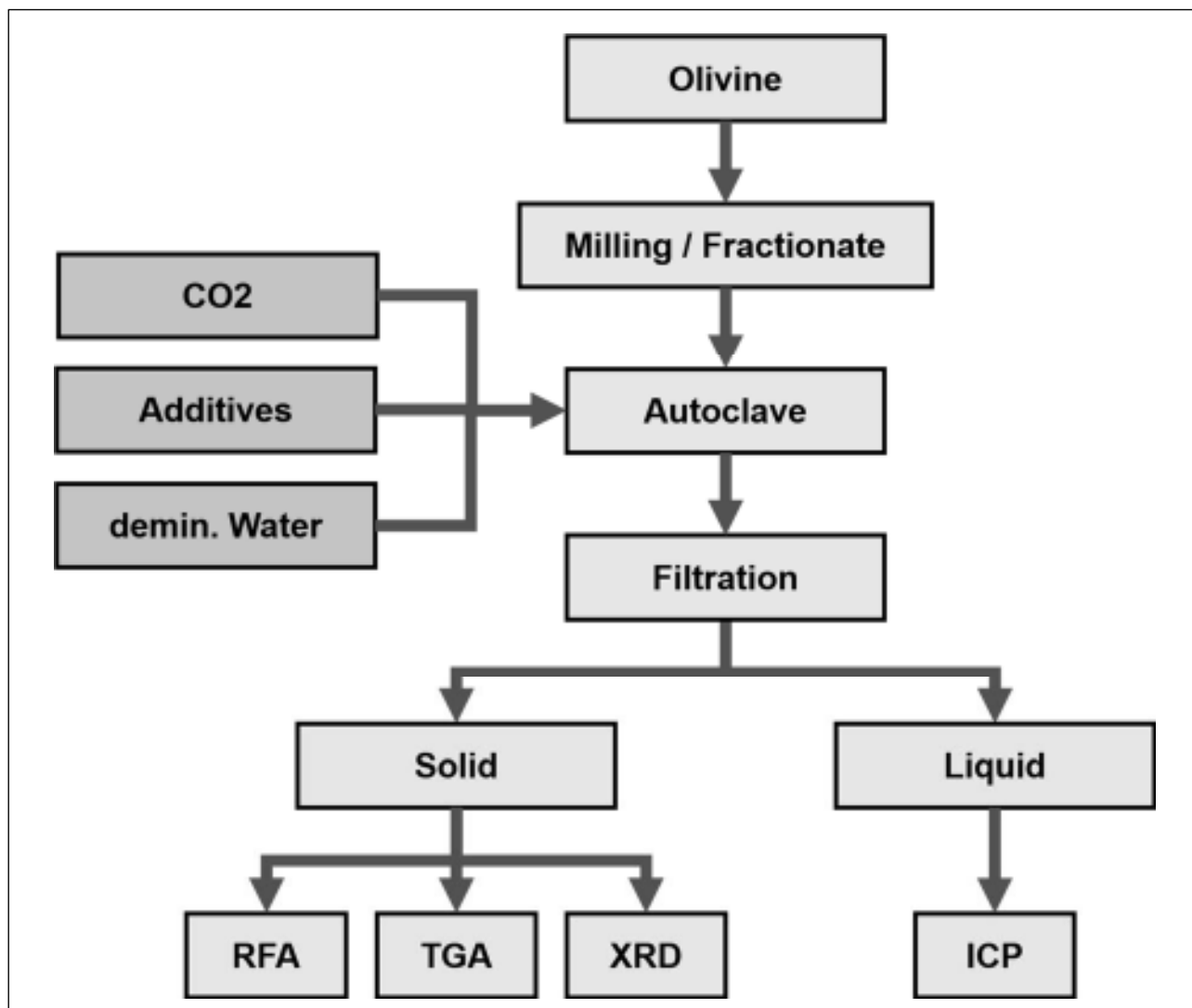


Figure 1: Procedure for experimental work and characterization of samples

Three particle size fractions < 20, 20 – 63 and 63 – 100 μm were tested after milling in an autoclave.

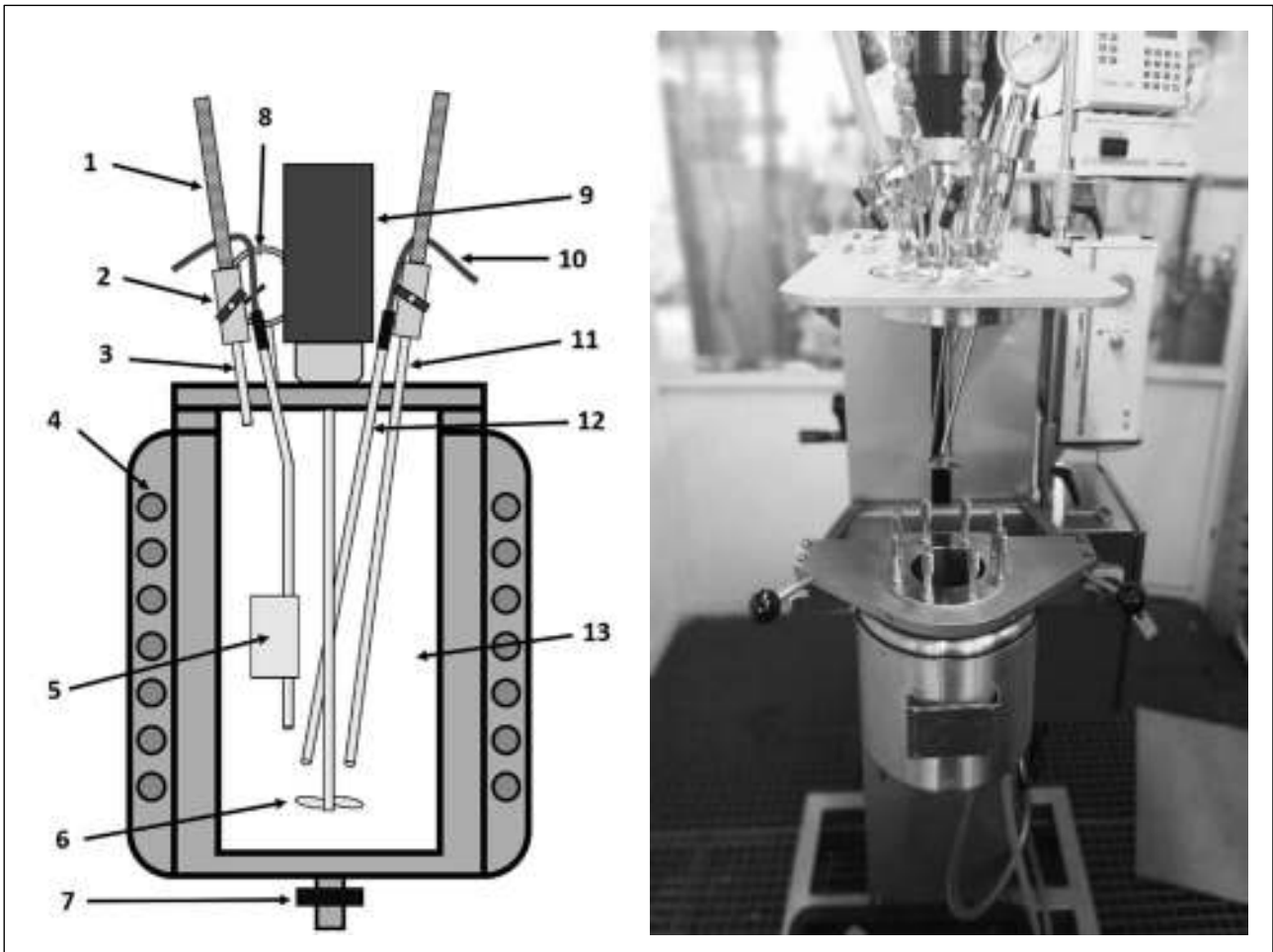


Figure 2: Sketch and picture of the autoclave: 1. pressure pipe (Stahlflex), 2. needle valve, 3. tube for gas exhaust; 4. reactor shell with heating and cooling; 5. temperature sample head; 6. propeller mixer; 7. outlet valve; 8 analog manometer; 9. motor for the magnetic coupled stirrer; 10. cable for the measurement cutting site; 11. gas inlet; 12. testing rode for pressure; 13. working volume

According to Ref. 8 (Turri et al.) and Ref. 9 (Stopic et al.) the carbonation tests have been carried out in the 1500 ml autoclave from Büchi Kiloclave Type 3E, Switzerland (as shown at Fig.2) at 175°C with 117 bar pure grade CO₂ in the presence and the absence of the additives such as sodium bicarbonate, oxalic acid and ascorbic acid in duration of 2 hours. An amount ranging from 100 to 300 g sample has been added to 1000 ml solution with mixing rate 600 revolution per minute in different experiments. After reaction, the liquid had very low contents of metal cations and analyzed via ICP OES analysis. Characterization of the solid products was restricted to the solid phase by TGA / DTA and XRD analyses.



2.3 Results and calculation of carbonation efficiency

Thermal decomposition of olivine and magnesia samples after carbonation under high pressure and filtration was performed in a muffle furnace at 850°C in 1 hour. Calculation of carbonation efficiency was made using the equation (6):

$$\text{Carbonation efficiency (\%)} = \frac{\text{mass loss (CO}_2\text{)} \text{ after thermal decomposition}}{\text{maximal loss of carbonate product}} \quad (6)$$

Thermal decomposition of formed magnesium carbonate and iron (III) carbonate was considered, as shown with equations (7) and (8):



The final calculation of the carbonation efficiency (Eq. 9) was derived via the Equation (6), (7), and (8):

$$\text{Carbonation efficiency [\%]} = 100 * \frac{m \text{ \%}}{\% \text{ MgO}_{\text{sample}} * \frac{M_{\text{CO}_2}}{M_{\text{MgO}}} + \% \text{ Fe}_2\text{O}_3 \text{ sample} * \frac{3 M_{\text{CO}_2}}{M_{\text{Fe}_2\text{O}_3}}} \quad (9)$$

Where:

m % – mass loss after thermal decomposition at 850 °C in 1 hour [%]

% MgO_{sample} and % Fe₂O_{3sample} – the content of oxides in used samples [%]

M_{MgO} and M_{Fe₂O₃} – molar mass, [g/mol]

The obtained results are shown in Table 2:

Table 2: Mass loss and carbonation efficiency for the Olivine sample and reference magnesia material

Material	Content of MgO [%]	Content of Fe ₂ O ₃ [%]	Theoretical mass loss during thermal decomposition (Eq. 9)	Experimental measured mass loss [%]	Real carbonation efficiency [%]
NedMag99	97,56	0.58	51.5	41.13* 37,07	79.86* 71.98
Olivine Steinsvik, Norway	41,81	7.77	28.0	12.5	44.56

*Experiment was performed in the presence of additives (sodium carbonate, oxalic and ascorbic acid)

The carbonation efficiency was amounted 71.98 % for NedMag99 sample in an autoclave (T = 175 °C, 1 L, 117 bar CO₂, 600 rpm, 2 hours) in the absence of additives of sodium carbonate, oxalic and ascorbic acid. In the presence of the previously mentioned additives the carbonation efficiency was increased to 79,86 % for NedMag99 and 44.56 % for Olivine Steinsvik. The presence of thin amorphous passivating silica rich layer might be a reason for a smaller carbonation efficiency.



Reactions proceeding through the formation of nano- to micron-scale dissolution channels provide a viable microscale mechanism in carbon sequestration practice [12], what shall be investigated in our future work.

3 Conclusion

The carbonation of different materials such as synthetic reference magnesite (MagNed99), and Steinsvik Olivine were successfully performed at 175 °C, 117 bar of CO₂ with 600 rpm in the presence of additives of sodium bicarbonate, oxalic acid and ascorbic acid in an autoclave in duration of 2 hours. The positive influence of additives on the carbonation efficiency was confirmed after a thermal decomposition of a solid product in a muffle furnace at 850 °C in 1 hour. The values of carbonation efficiencies were amounted after a calculation of 79.86 % for reference sample NedMag99 and 44.56 % for olivine Steinsvik in the presence of additives at the previous mentioned conditions, respectively. This work begun the research study related to mechanism and kinetics of carbonation and deeply analysis of formed products (magnesium carbonate and silica).

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