

Article

Mechanism of Nickel, Magnesium, and Iron Recovery from Olivine Bearing Ore during Leaching with Hydrochloric Acid Including a Carbonation Pre-Treatment

Carlos Matus ¹, Srečko Stopić ^{2,*}, Simon Etzold ³, Dario Kremer ⁴ , Hermann Wotruba ⁴, Christian Dertmann ², Rainer Telle ³, Bernd Friedrich ² and Pol Knops ⁵

¹ Refratechnik Cement GmbH, Sales Department, Rudolf-Winkel-Strasse 1, 37079 Gottingen, Germany; carlos.matus@refra.com

² IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Intzestrasse 3, 52056 Aachen, Germany; cdertmann@metallurgie.rwth-aachen.de (C.D.); bfriedrich@metallurgie.rwth-aachen.de (B.F.)

³ Department of Ceramics and Refractory Materials, GHI-Institute of Mineral Engineering, RWTH Aachen University, Mauerstrasse 5, 52064 Aachen, Germany; etzold@ghi.rwth-aachen.de (S.E.); telle@ghi.rwth-aachen.de (R.T.)

⁴ AMR Unit of Mineral Processing, RWTH Aachen University, Lochnerstrasse 4-20, 52064 Aachen, Germany; kremer@amr.rwth-aachen.de (D.K.); wotruba@amr.rwth-aachen.de (H.W.)

⁵ Green Minerals, Rijksstraatweg 128, NL 7391 MG Twello, The Netherlands; pol@green-minerals.nl

* Correspondence: sstopic@metallurgie.rwth-aachen.de; Tel.: +49-241-80-95860

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Abstract: This work continues on from previous studies showing that mineral sequestration by carbonation of magnesium or calcium silicates under high pressure and high temperature can be successfully carried out by processing in an autoclave. The paper is focused on the influence of experimental parameters on avoiding scale formation during pre-treatment in an autoclave and a subsequent leaching. Amorphous silica and magnesite, respectively, were the main reaction products in a carbonation of olivine under high pressure conditions in an autoclave. In addition, the examined peridotites may be accompanied by small to medium amounts of nickel or other metals, the recovery of which will be investigated in the present study: Extraction of metals such as nickel, iron, and magnesium from olivine bearing ore using hydrochloric acid under atmospheric pressure was studied between 50 and 90 °C in 1 h. The obtained results have shown maximal leaching efficiency of about 35% for Ni, Fe, and Mg under atmospheric pressure, in comparison to more than 60% obtained under the same conditions after a carbonation pre-treatment in an autoclave. Silica gel was formed during leaching without a pre-treatment of peridotite blocking the leaching process, which is not the case for the pre-treated material. The influence of temperature, reaction time, particle size and pre-treatment of peridotite in an autoclave during carbonation at 175 °C and 71.5 bar was studied. A new mechanism model for metal extraction from olivine-bearing ore by avoiding silica gel formation during leaching with hydrochloric acid including a carbonation pre-treatment is proposed. This study explains additionally a behavior of metals such as nickel, magnesium, and iron during a carbonation of olivine bearing ore and leaching of a carbonated solid product.

Keywords: olivine; carbonation; recovery; nickel; magnesium; iron; leaching

1. Introduction

Olivine is a magnesium–iron silicate with the chemical formula $(\text{Mg, Fe})_2\text{SiO}_4$. A distinction is made between magnesium olivine (Mg_2SiO_4) with the name Forsterite and iron olivine (Fe_2SiO_4)

with the name Fayalite. Both types of olivine have a different degree of conversion for the maximum degree of carbonation. Olivine is formed deep in the upper mantle and occurs in mafic and ultramafic magmatic rocks [1,2]. In terms of structure, olivine can be described as a hexagonal dense spherical packing of oxygen atoms. Silicon is found in smaller tetrahedral gaps between four oxygen atoms. The Fe^{2+} or Mg^{2+} ions take place in the larger octahedral gaps with six oxygen atoms as their nearest neighbors. Forsterite has a high melting point of 1890 °C. The melting point of the iron-bearing olivine (fayalite), however, is only about 1205 °C. Olivine exhibits a green color whose strength increases with the iron content. For simplicity the input material for our process is named olivine in the following, although it is a peridotite with ~70 wt.% olivine content.

Kremer et al. [3] investigated the possible mineral input materials such as olivine and basalt for the process of mineral sequestration through the carbonation of magnesium or calcium silicates under high pressure and high temperatures in an autoclave. The choice of input materials for the carbonation that are covered by this study represents more than 50% of the global olivine production. Reaction products of a carbonation are amorphous silica and magnesite or calcite, respectively. The carbonation experiments were performed in water solution under high pressure conditions. During carbonation a silica passive layer was formed by nanosilica particles, which decreases scale formation.

Turri et al. [4] performed a flotation of chromite as pre-treatment of olivine before carbonation for CO_2 sequestration in order to increase carbonation efficiency and decrease the toxicity of the solution because of the presence of Cr^{6+} -ions. The mixed crystal is mainly used in the metallurgical field for different applications. Because of its refractory properties, Mg-based compounds serve the furnace construction. High interest was developed for an using of the produced nanosilica particles. The main problem was how to separate a produced silica from a magnesite.

In a method by Olerud [5] for manufacturing silica, the leaching of natural silicates (olivine) is performed with hydrochloric or other mineral acids at 110 °C, followed by draining, drying and possibly grinding up residues of the product obtained (US Patent 5.780.005). In order to obtain spherical silica particles with a controlled particle size and surface characteristics, forsterite (Mg_2SiO_4) was used with the highest possible degree of purity (approx. 97 wt.%). The product is colloidal amorphous silica in the form of a gel. The silica gel is separated from the liquid by pressure filters, washed clean of acid remains, dried, and ground.

The extraction of silica gel and magnesium compounds from olivine is proposed by Hansen and Zander [6], who used sulfuric acid in a thermal treatment at temperatures between 150 and 400 °C (European Patent EP 1373 139 B1) for 4–12 h.

Crundwell [7] has proposed a new mechanism of dissolution of forsterite, olivine, and minerals of the orthosilicate group, considering the change in order of reaction at higher pH values. The acceleration of the rate of dissolution by organic acids and the retardation of the rate by dissolved silica and carbon dioxide are also predicted. The mechanism predicts a change in the interfacial potential difference at the same pH value the order of reaction changes. This prediction is verified by measurements of the zeta potential, which reflects the predicted change in surface potential at a pH of approximately 6. The proposed mechanism provides a framework for the interpretation of the correlation between the rate of dissolution of the orthosilicates and the exchange rates of water in the inner sphere of the corresponding metal aqua-ion.

Oelkers et al. [8] suggested that the major factors influencing forsteritic olivine dissolution rates are pH value, temperature and mineral–fluid interfacial surface area. They suggested that the effects of aqueous inorganic and organic species are relatively limited and might be attributed, at least partially, to their influence on pH value of an aqueous solution. Each of these mentioned factors influences the application of forsterite dissolution to enhanced weathering efforts, mineral carbonation, and the low-temperature generation of hydrogen via the oxidation of its divalent iron.

Stopic et al. [9] have primarily shown the reaction path of direct forsterite carbonation for a synthesis of magnesium carbonate in an aqueous solution without any deeper consideration of the formed silica particles in the presence of additives: sodium bicarbonate, oxalic acid, and ascorbic

acid in a 0.25 L horizontal autoclave (Parr Instruments, Moline, IL, USA). First, gaseous carbon dioxide dissolves in aqueous solution. Simultaneously, forsterite is dissolved in aqueous solution forming aqueous silicic acid, followed by precipitation as amorphous silica which is a by-product, and lastly, magnesium ions and carbonate form magnesite. Formation of magnesium carbonate has been confirmed by X-ray diffraction (XRD) analysis.

Furthermore, Stopic et al. [10] reported a synthesis of nanosilica via carbonation of olivine using particle size fraction between 20 and 63 μm with a solid/liquid ratio of 1:10 at 175 °C and partial pressure of CO_2 of more than 100 bar in an 1.1 L autoclave, in the presence of additives such as sodium bicarbonate, oxalic and ascorbic acid. The influence of the solid/liquid ratio, particle size, stabilizing pressure and the amount of additives on the carbonation degree was studied. In comparison to ultrasonic spray pyrolysis, sol-gel and carbonation method via bubbling CO_2 gas into calcium ions dispersing in methanol solution under atmospheric pressure, this synthesis of nanosilica was performed in a water solution in a closed reactor. In this autoclave, high-pressure conditions above 100 bar prevail, avoiding the formation of silica gel, which blocks the metal extraction. An increase of stirring speed from 600 to 1800 rpm raises the pressure from 120 to 170 bar, leading to an increase of silica production because of a removal of passivated silica formed layer at the forsterite particles' surface. The precipitated silicate particles were separated at pH values between 7.32 and 8.57. Separation of produced silica from magnesium carbonate appeared as an unsolved problem for the future application.

During a study of the kinetics and mechanism of mineral carbonation of olivine for CO_2 sequestration, Wang et al. [11] found that the addition of sodium bicarbonate can dramatically increase the ionic strength and aid the dissolution of silicon to temporarily aqueous H_4SiO_4 followed by decomposition to amorphous silica and consequently the removal of Si-rich layer. The aqueous silicon was not stable and can be decomposed into amorphous silica, which was extensively observed in the aqueous solution after carbonation and settled down for more than one month at room temperature. CO_2 sequestration with olivine as feedstock was performed in a rocking batch autoclave at 175 °C and 100 bar in an aqueous solution and a CO_2 -rich gas phase from 0.5 to 12 h, as shown by Turri et al. [12]. Characterization of the recovered solids revealed that carbonates predominate in particle size ranges below 40 μm . The larger residue fraction of the final product after carbonation consisted mainly of unreacted olivine, while silica is more present in the form of very fine spherical 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 to obtain maximum carbonation, which leads also to a complete formation of silica. The previous mentioned experiments by Turri et al. [12] have performed in a rotary autoclave ensuring an information about chemical composition of obtained solution and a way to remove chromium from final solution during carbonation of olivine. These results were used as an initial point for the planning of experiments in the work of Stopic et al. [9,10], but information about metal recovery from solution was still missing.

A novel mineral processing approach using carbon dioxide to promote mineral alterations that lead to improved extractability of nickel from olivine was reported by Santos et al. [13]. Carbonation pre-treatment leads to mineral liberation and concentration of metals in physically separable phases. In a first processing step, olivine is fully carbonated at high carbon dioxide partial pressures (35 bar) and optimal temperature (200 °C) in a 1.1 L Büchi Ecoclave continuously stirred tank reactor with the addition of pH buffering agents producing powdery product with a high carbonate content. The main products of the carbonation reaction include quasi-amorphous colloidal silica, chromium-rich metallic particles, and ferro-magnesite ($(\text{Mg}_{1-x}\text{Fe}_x)\text{CO}_3$). Carbonated olivine was subsequently leached using an array of inorganic and organic acids to test their leaching efficiency. Compared to leaching from untreated olivine, the percentage of nickel extracted from carbonated olivine by acid leaching was significantly increased. The prevention of silica gel formation and the mechanism of metal extraction was not discussed by Santos et al. [13].

Generally, the previously mentioned results studied carbonation of olivine [3–13], but an information about an extraction of nickel, magnesium and iron from the obtained solution is missing.

A flowchart of new combined process of carbonation of olivine and a subsequent leaching can be a new strategy for metal recovery.

This paper deals with the mechanism of metals extraction from olivine using hydrochloric acid during the formation of silica gel and the possibility to avoid silica gel formation. Analysis of the pre-treatment method using higher carbon dioxide partial pressures of 71.5 bar, higher working volume of 8.0 L, a minimal carbonation reaction time of 4 h and lower temperature of 175 °C, shall explain the behavior of metals and relationship with the formation of silica during treatment. The main aim of this study is to offer a new reaction mechanism model for the metal extraction explaining the partial steps of this strategy.

2. Materials and Methods

2.1. Material Analysis Methods

The input material for all performed experiments and processes described in the present study constitutes Norwegian olivine-bearing ore, ground and fractionated into several grain sizes between <20 and 150 µm. Table 1 shows the chemical composition of the various olivine fractions as characterized by X-ray fluorescence (XRF) technique, type PW2404 (Malvern PANalytical, Malvern, UK). Milling was performed using Roller Mill, Type LWBP 2/2 (Karl Merz Maschinenfabrik GmbH, 1972 (year of manufacture), Heschingen, Germany). Sieving was performed using Sieving Maschine, Type Prüf 86 (Siebtechnik GmbH, Mühlheim an der Ruhr, Germany). Although a statistical analysis was not performed, a chemical analysis of different particle size fractions shown in Table 1, has revealed minimal deviations in the composition of the investigated nickel oxide, magnesium oxide, and iron (III) oxide in initial sample.

Table 1. Chemical composition of the Norwegian olivine fractions after grinding and sieving.

Compound (wt.%)	<20 µm	20–63 µm	100–150 µm
SiO ₂	47.91	47.31	47.72
Al ₂ O ₃	0.58	0.47	0.42
Fe ₂ O ₃	7.02	7.41	7.38
CaO	0.72	0.17	0.11
MgO	42.49	43.58	43.42
MnO	0.11	0.12	0.11
Cr ₂ O ₃	0.41	0.38	0.38
NiO	0.41	0.39	0.41
Others	0.35	0.17	0.05

Table 2 shows the mineralogical composition of the feed material for the investigated leaching process, which mainly consists of olivine, orthopyroxene, lizardite, and chlorites. Nickel can be situated in the olivine, amphibole or as nickel spinel. As the percentage of the contained amphibole and spinel group is very low in the analyzed feed sample, it can be presumed that at least a part of the nickel oxide is embedded in the olivine crystal lattice.

Because of nickel bonding in crystal structure the liberation of nickel from this packing is very difficult. The olivine, which is according to mass most dominant reacts with acid and CO₂ under high pressure forming metal carbonate.

Semi-automated mineralogical analyses were performed by applying a Quanta 650-F QEMSCAN© (FEI/Thermo Fischer, Hillsboro, OR, USA) scanning electron microscope (SEM) at the Institute of Applied Mineralogy and Economic Geology, RWTH-Aachen University. Polished thin sections and polished sections were analyzed after carbon coating. The measurements were conducted with an acceleration voltage of 25 kV and a fixed sample current of 10 nA. The surface of each sample section was scanned with a spatial resolution of 5 µm. Back scatter (BSE) intensities and individual X-ray spectra were

recorded for each pixel with a 4-quadrant BSE detector and two DualXFlash 5030 SDD (Bruker AXS, Karlsruhe, Germany) energy dispersive x-ray spectrometers (EDX). Phase assignment was carried out by comparison of spectral data obtained for each pixel with library information using the iDiscover (Version 5.3.2.501, FEI/Thermo Fisher, Hillsboro, OR, USA) software suite. Automated image analysis was applied to phase maps to compute quantitative mineralogical and textural parameters. The modal composition of each sample in volume (vol.%) was calculated from the volumetric abundance of each mineral phase. Particle size calculations were conducted by measurement of the diameter of the virtual sphere with equivalent perimeter length assigned to each individual target phase. Particle populations were obtained by segmentation of the target minerals or mineral assemblage from QEMSCAN® phase maps.

Table 2. Mineralogical composition of the used ore (QEMSCAN®—“Quantitative Evaluation of Minerals by Scanning Electron Microscope”).

Mineral	Content (vol.%)
Lizardite	6.24
Biotite	0.06
Chlorites	3.40
Spinel Group	0.33
Amphibole	0.04
Orthopyroxene	13.55
Hornblende	0.07
Olivine	71.52
Ca-Pyroxene	0.96
Other Minerals	1.14
Unclassified	2.69

The mineral association for the particle size fraction 20–63 μm , which was analyzed by QEMSCAN® shows that olivine, pyroxenes, chlorites and the spinel group are mostly liberated, which is visible in the Figure 1 with association of mineral with background representing the liberation degree. Lizardite and the spinel group are associated with olivine by 23 vol.% or 5 vol.%, respectively, whereas other classified minerals are associated with olivine less than 5 vol.%.

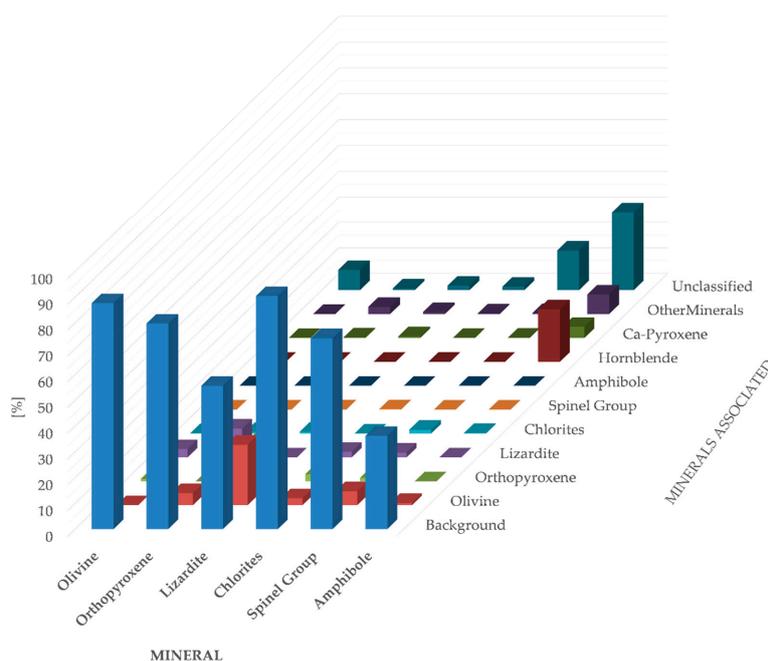


Figure 1. Mineral Association of the used olivine bearing ore (QEMSCAN®).

2.2. Leaching of Olivine Bearing Ore without Carbonation Pre-Treatment

The focus of this work is the investigation of the extraction of nickel, magnesium and iron from olivine-bearing ore by leaching. The experimental parameters that have been changed in order to determine the influence on the leaching efficiency are shown in the test matrix (Table 3). The test parameters such as solid/liquid ratio, atmospheric pressure, and hydrochloric acid concentration (except experiment 8) for the leaching process were kept constant. In the case of temperature, time, stirring speed and particle size, the parameters were changed. Figure 2 shows the experimental setup for leaching, washing and filtration. Experiments were performed in a 2 L laboratory reactor LR-2.ST (IKA Werke GmbH, Staufen im Breisgau, Germany) with a subsequent filtration using Vacuum Pump (Welch Iilmvac, Ilmenau, Germany), as shown in Figure 2).

Table 3. Leaching parameters for the executed experiments with and without carbonation pre-treatment.

Experiment	T (°C)	t (min)	Particle Size (µm)	Concentration (mol/L)	Leaching Agent
Leaching (without carbonation pre-treatment)					
1	50	30, 60	<20	1	HCl
2	50	30, 60, 90	20–63	1	HCl
3	50	30, 60, 90, 120, 150, 180	100–150	1	HCl
4	80	30, 60, 90	100–150	1	HCl
Leaching (after carbonation pre-treatment)					
5	50	60, 120, 180, 240	20–63	1	HCl
6	80	60, 120, 180	20–63	1	HCl
7	90	60, 120, 180, 240	20–63	1	HCl
8	50	60, 120, 180	20–63	2	HCl

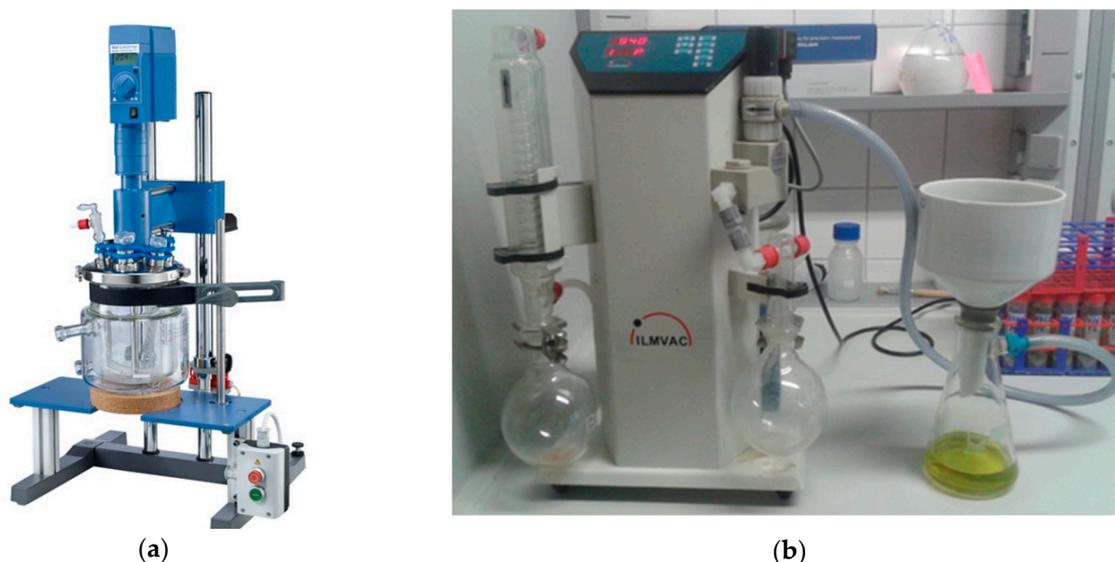


Figure 2. (a) Leaching laboratory reactor; (b) Filtration unit.

The 1 M hydrochloric acid solution was prepared in a 1 L measured weighed flask, followed by mixing with olivine in the required particle size in the reactor shown in Figure 2a to obtain a solid/liquid ratio of 1:10. The initial pH value was measured for monitoring and to enable comparison with the pH value after leaching. The desired temperature was set and the titanium stirrer was adjusted to the respective stirring speed of 300 rpm. The leaching process took a total of up to 240 min, with samples being taken periodically. The sampling during leaching was performed each 60 min. After completion of the leaching process, the leaching unit was cooled down to room temperature. Subsequently, filtration and neutralization with distilled water were carried out. This was performed in a built-in filtration system as shown in Figure 2b. A suitable filter paper was installed in the stage hopper, so that filtration can take place through the suction bottle and stage funnel, which is connected

to the vacuum pump. The sampling solution had to be poured into the stage funnel and the vacuum pump switched on.

2.3. Leaching of the Carbonated Olivine

The treatment of olivine was performed using firstly the operations such as milling, sieving, and carbonation under high pressure conditions with an additional filtration and chemical analysis of solid and liquid as reported by Stopic et al. [9,10]. The carbonation tests have been carried out in the 9.9 L autoclave (Hastelloy C22 pressure reactor) of a kiloclave Type 3E (Büchi) with electric heating and water cooling (as shown in Figure 3) at 175 °C with 71.5 bar pure grade CO₂ in the presence of additives, such as sodium bicarbonate, oxalic acid, and ascorbic acid.

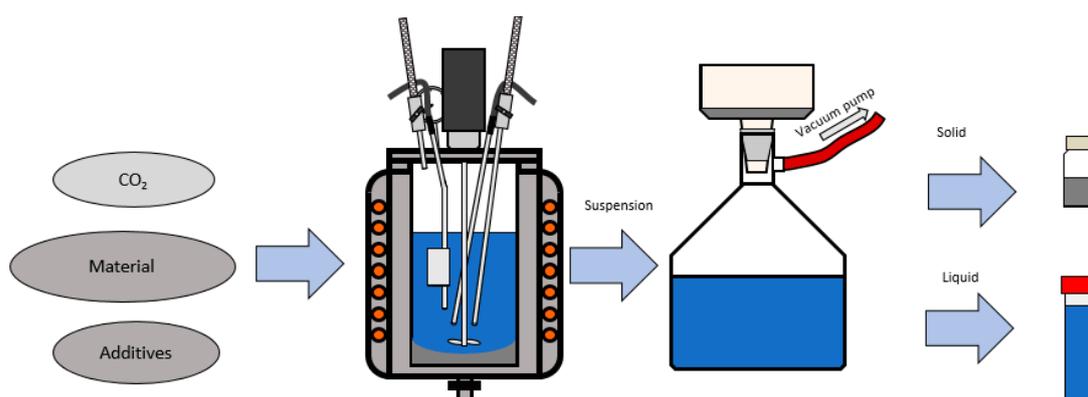


Figure 3. Carbonation process of olivine and a filtration with a sampling.

As visible in Table 3 for determination of carbonation as a suitable pre-treatment method for leaching, only the particle size fraction 20–63 µm has been examined. An amount of 1000 g per sample has been added to 8.0 L water solution with a mixing rate of 600 rpm in different experiments. Pure CO₂ was injected, followed by heating up to 175 °C. The change of temperature and pressure during heating and cooling down has been monitored. Carbonation was performed for a residence time of 4 h at 175 °C. After this reaction time for carbonation, the solution was cooled to 80 °C and the pressure was decreased to the atmospheric values. After opening the cover of the autoclave, the solution was filtrated in order to separate the solids from the solution (Figure 4). To investigate the mineralogical composition prior and subsequent to the carbonation pre-treatment, X-ray diffraction (XRD) technique has been applied (D8 Advance device in Bragg-Brentano geometry, with LynxEye Detector, CuKα tube, and nickel filter; Bruker AXS). The characterization of liquid products was performed using the ICP-OES analysis (SPECTRO ARCOS, SPECTRO Analytical Instruments GmbH, Kleve, Germany). The evolution of the mineralogical composition of the solid product after carbonation and the amount of stored CO₂ were investigated by XRD and TGA/DSC in previous studies [6,9,10]. The focus of this study lies in the leaching process, therefore the carbonation is not discussed further.

Leaching of formed magnesium, nickel and iron carbonate with hydrochloric acid can be explained by Equations (1)–(3).

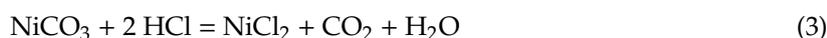
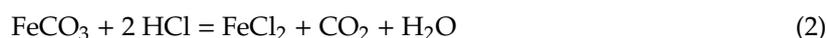
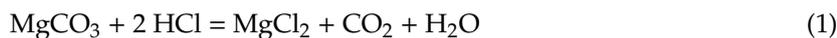




Figure 4. (a) Filter cake and (b) obtained solution during carbonation.

3. Results

3.1. Material Analysis after Carbonation as a Pre-Treatment Step

To evaluate the overall capability of the carbonation process, an experiment was performed using Norwegian olivine (20–63 μm) at 175 $^{\circ}\text{C}$, CO_2 -pressure of 71.5 bar, 120 min, 600 rpm, in a 9.9 L autoclave (as shown in Figure 3) in the presence of additives of sodium carbonate, oxalic, and ascorbic acid. Figure 5 shows the XRD pattern of the initial sample before carbonation and the carbonation product.

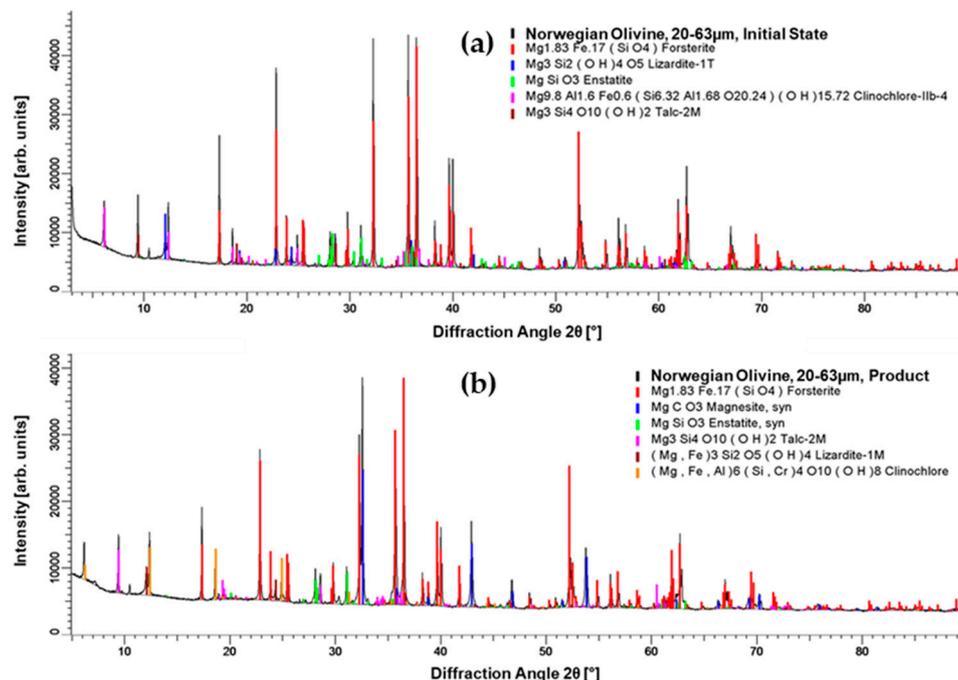
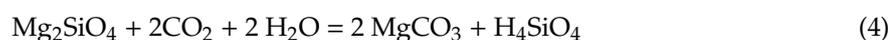


Figure 5. X-ray diffraction (XRD) analysis of Norwegian olivine samples: (a) initial state and (b) carbonation product.

The most considerable mineralogical phase amounts in the initial sample are forsterite, enstatite, lizardite, clinocllore and talc, as reported by Kremer et al. [3]. Apparently, after carbonation the main mineralogical phase changes from forsterite to magnesite, whereas the further components undergo

only minor modification due to the autoclave process. The presence of magnesite after processing indicates the successful carbonation of the input material.

The content of enstatite, lizardite and talc was not significantly changed, pointing out that these mineralogical phases show less reactivity within the performed process than forsterite. The carbonation process was explained with the following chemical reactions, as shown with Equations (4) and (5):



The presence of magnesite and silica was confirmed using the SEM analysis (ZEISS GeminiSEM 500, Carl Zeiss AG, Oberkochen, Germany) of the solid product, as shown in Figure 6.

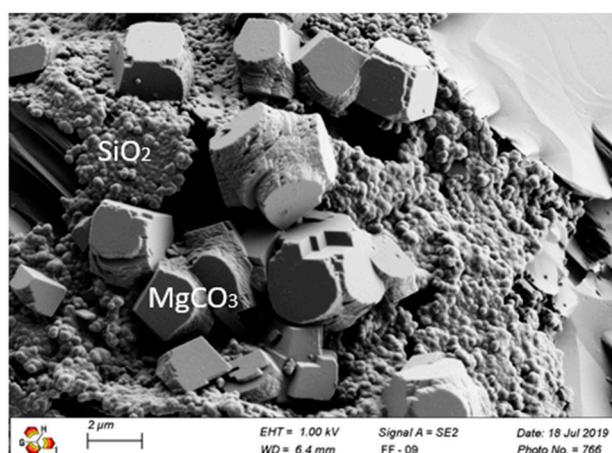


Figure 6. Typical scanning electron microscope (SEM) analysis of carbonated product at 175 °C, 71.5 bar and 4 h (20–63 µm).

SEM analysis has confirmed that magnesite crystals (2–5 µm) and very small particles of amorphous SiO₂ (100–200 nm) are formed as rhombohedrons or hexagonal prisms at the surface of partially carbonated magnesium silicate. This silica agglomerated islands and magnesium carbonate might constitute a barrier for the carbonation. Although the formed silica is situated in water solution, the formation of silica gel and scale was not detected under these high-pressure conditions.

After the carbonation process, the obtained product is filtered using a vacuum pump, a stage funnel and a suction bottle. The filtration time correlates with the particle size. The smaller the particles, the longer the filtration process, because the very fine particles clog the pores of the filter paper so that the filtration process was decelerated.

The final pH value of solution after carbonation was amounted 8.57. The chemical composition of solution from the autoclave after filtration confirms that the leaching efficiency of Ni, Mg, and Fe in water under high pressure is smaller than 1 wt.%, which is minimal recovery (Table 4).

Table 4. Chemical composition of solution after carbonation.

Element	Ni	Mg	Ca	Fe	Al	Si	Mn
Concentration (mg/L)	1.27	76.2	<1	2.92	<1	74.8	<1

3.2. Leaching of Olivine Bearing Ore without Carbonation Pre-Treatment

The first leaching experiments with hydrochloric acid but without a pre-treatment step were performed using parameters from Table 3, in order to study extraction of metals such as nickel, iron

and magnesium. First the effect of the particle size on the leaching efficiency was investigated. Figure 7 shows the correlation of smaller particle size with increasing efficiency.

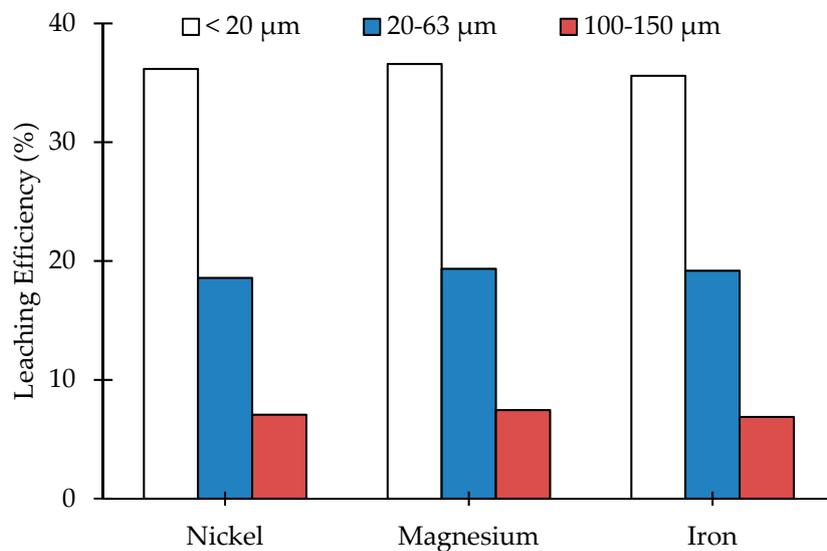


Figure 7. Leaching efficiency depending on particle size, 50 °C, 60 min, 1 M HCl and 300 rpm.

The leaching efficiency significantly increases from ~7% in the coarsest fraction of 100–150 μm for all three investigated elements up to ~35% in the fraction <20 μm.

An increase of the leaching time from 30 to 180 min (Figure 8) for the fraction between 100 μm and 150 μm leads to an increase of the leaching efficiency of magnesium from 4% to 21%, which is the case for nickel and iron. Because of similar metal extraction, the selectivity of the leaching process is not further considered in these experiments.

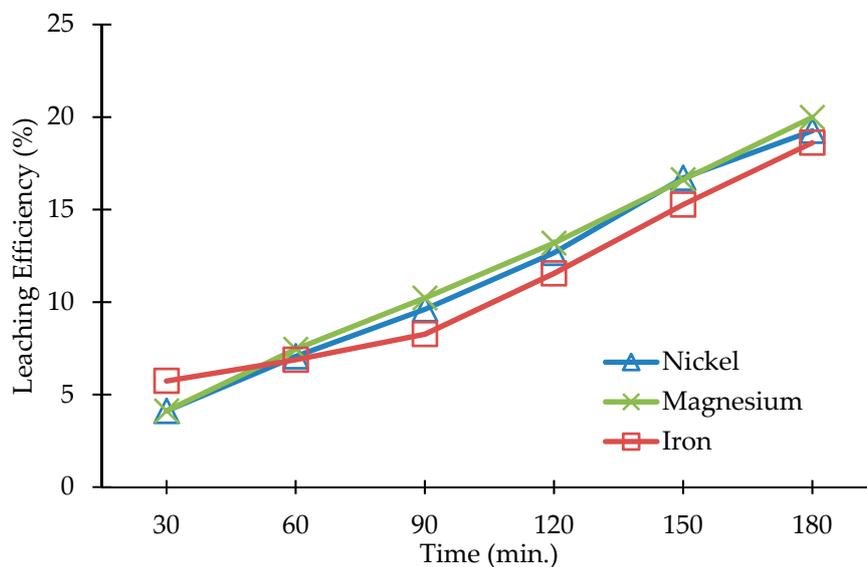


Figure 8. Leaching efficiency depending on leaching time, 100–150 μm, 50 °C, 1 M HCl and 300 rpm.

Figure 9 compares the leaching efficiency for the three metals with regard to the influence of the temperature. At a temperature of 50 °C a leaching efficiency of <10% can be observed, whereas at a temperature of 80 °C, leaching efficiencies of >30% for nickel and >40% for magnesium and iron could be achieved.

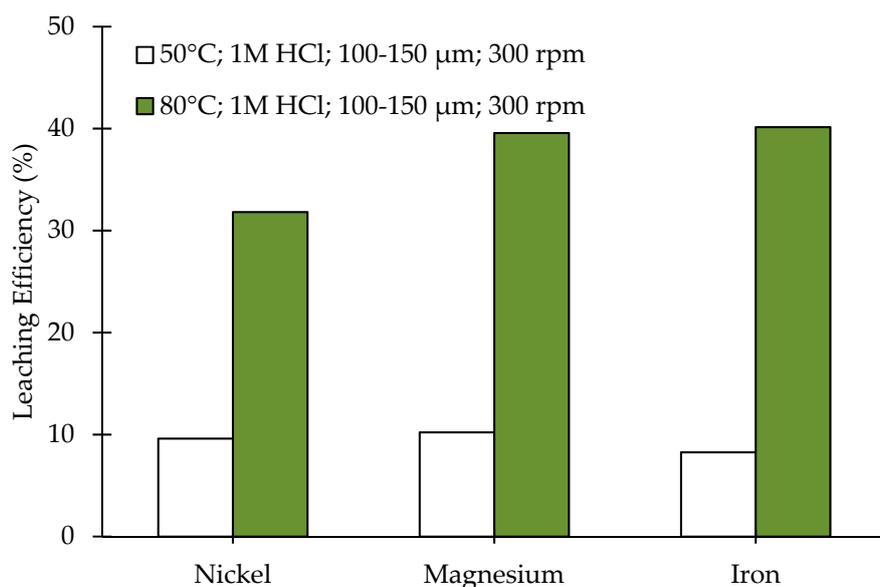
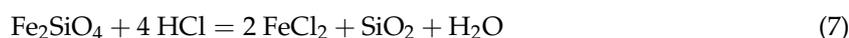
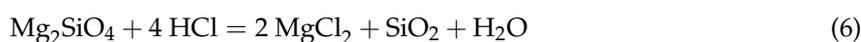


Figure 9. Leaching efficiency depending on a leaching temperature, 100–150 μm, 90 min, 1 M HCl and 300 rpm.

The mechanism of metal transfer from olivine to solution during the leaching process is presented using the following chemical reactions, as shown with Equations (6)–(8):



Silica gel formation was expected during the acidic leaching tests with regard to metal extraction after one hour [10–12]. It was observed that the temperature is an important factor in the formation of silica gel. In the experiments with a process temperature of 80 °C, less silica gel was formed than in the test with 50 °C, which means that an increase of temperature leads to the prevention of its formation. Due to the formation of silica gel, the filtration process is extremely slowed down, so the filtration was carried out overnight. It also turned out, that the strong silica gel formation did not occur until one hour after the start of the test, but an increase of leaching time above 60 min leads to its formation.

Silica gel represents an amorphous and porous form of silicon dioxide consisting of an irregular tridimensional framework of alternating silicon and oxygen atoms with nanometer-scale pores as reported by Zulfiqar et al. [14]. The dissolution of silicon from quartz or amorphous silica involves hydrolysis in the access of water to form monosilicic acid, as shown with Equation (9).



Silica gel formation is not only dependent on temperature, but also on pH value of the solution, which amounted to 2.36 in these experiments.

3.3. Leaching of the Carbonated Olivine

The leaching procedure was performed as described in Section 2.3. The carbonated material (filter cake) was leached similar to the initial olivine samples as it can be seen in Table 3.

The positive effect of increasing leaching time on the leaching efficiency of carbonated olivine is shown in Figure 10.

The leaching of the carbonated olivine product (particle size between 20 and 63 μm) with 1 M and 2 M hydrochloric acid was performed at different temperatures between 50 and 90 °C and different

leaching times (Figure 11) in order to establish the influence of the temperature and concentration of the leaching agents. As mentioned before the pH value after carbonation process was 8.57. During leaching process between 50 and 90 °C in duration from 60 to 180 min, the positive influence of temperature on the pH increase was found with values between 0.46 and 2.88, which confirms accelerated reaction kinetics.

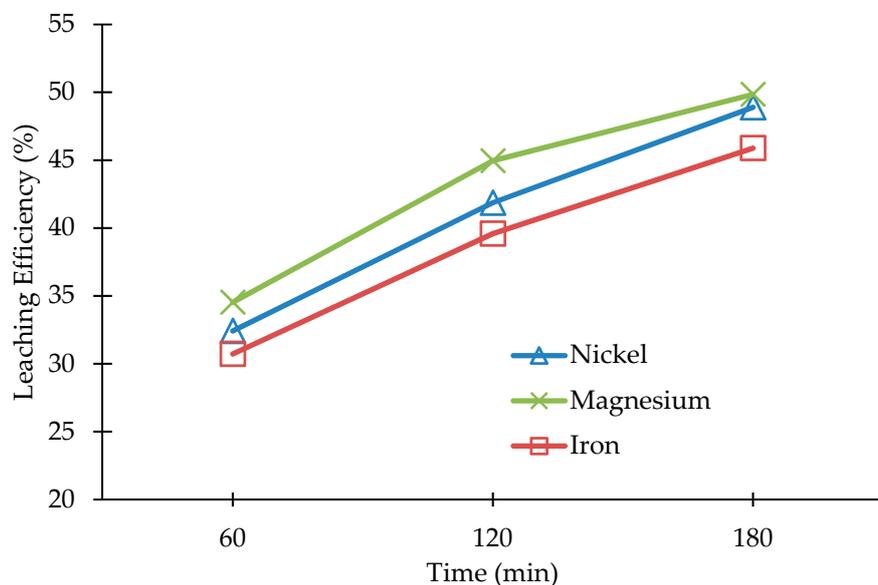


Figure 10. Leaching efficiency of carbonated olivine depending on leaching time, 20–63 μm , 50 °C, 1 M HCl and 300 rpm.

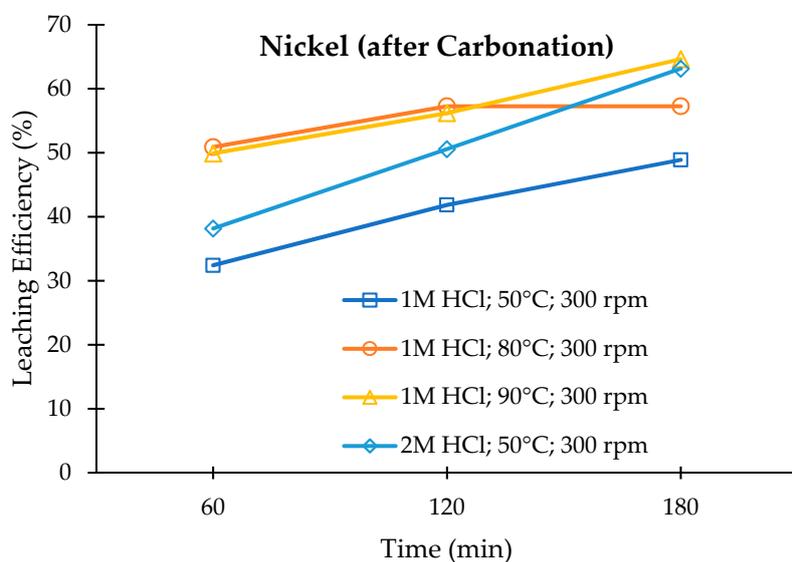


Figure 11. Leaching efficiency of nickel from a carbonated olivine depending on concentration of hydrochloric acid and reaction temperature for the fraction 20–63 μm .

A leaching process of the combined optimum parameters (20–63 μm , 90 °C, 1 M HCl, 300 rpm, and 180 min) resulted in leaching efficiencies of minimum 60%. An increase of concentration of hydrochloric acid from 1.0 to 2.0 mol/L at 50 °C increases the leaching efficiency of nickel, iron, and magnesium from carbonate fraction (20–63 μm) between 60 and 180 min, as shown at Figures 12–14. Further analysis of the mentioned Figures 11–13 has shown that an increase of temperature from 50 °C to 90 °C increases to metal extraction under previously reported conditions.

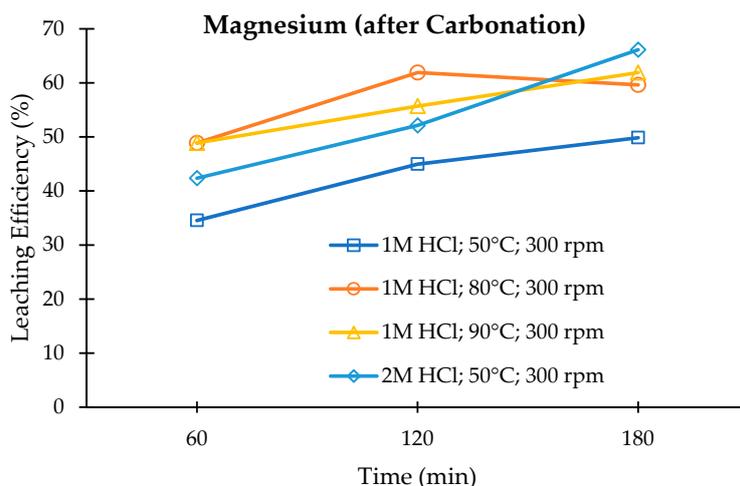


Figure 12. Leaching efficiency of magnesium from a carbonated olivine depending on concentration of hydrochloric acid and temperature for the fraction 20–63 μm.

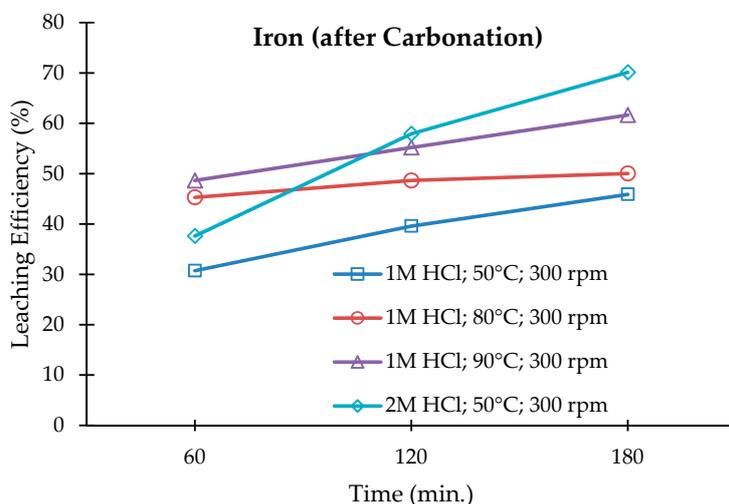


Figure 13. Leaching efficiency of iron from a carbonated olivine depending on concentration of hydrochloric acid and temperature for the fraction 20–63 μm.

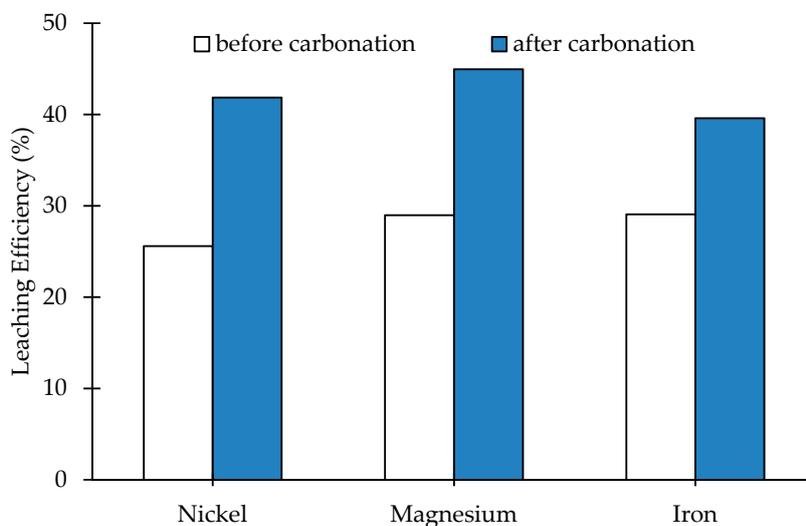


Figure 14. Comparison of the leaching efficiency of olivine without carbonation and with olivine with carbonation as a pre-treatment step, 20–63 μm, 50 °C, 120 min, 1M HCl and 300 rpm.

4. Discussion

Dissolution of the olivine bearing ore (<20 μm , 20–63 μm and 100–150 μm) was studied with hydrochloric acid between 50 and 90 $^{\circ}\text{C}$ in duration of 30–180 min in order to establish the leaching efficiency of nickel, magnesium and iron. A positive influence of the decreased particle size (from 100–150 μm to fraction below 20 μm), increased reaction time, and temperature on the leaching efficiency was found in all cases. After one hour of leaching, silica gel appeared, which blocks the leaching process at 50 $^{\circ}\text{C}$. In order to avoid a gel formation and to increase metal extraction a carbonation of olivine was performed at 175 $^{\circ}\text{C}$ and 71.5 bar carbon dioxide in water solution in the presence of additives, producing amorphous silica (100–200 nm) and magnesium carbonate (2–5 μm). The carbonation efficiency amounted 24.94%, with minimal transfer of metals in solution from initial olivine bearing ore. Especially, a carbonation pre-treatment in an autoclave leads to an increased leaching efficiency from 25–30% to 40–45% at 50 $^{\circ}\text{C}$ for all recovered metals. The leaching of carbonated olivine with 1 M hydrochloric acid at temperatures between 50 and 90 $^{\circ}\text{C}$ for fraction between 20 and 63 μm leads to maximal leaching efficiency minimum 60% for Fe, Ni and Mg in 1 h.

A comparison of the leaching efficiencies for the investigated metals before carbonation and with carbonation as a pre-treatment step are shown in Figure 14.

According to a literature review [9–13] and our obtained results, a new recovery mechanism for metals from olivine is proposed during the carbonation under high pressure in an autoclave with a subsequent leaching in hydrochloric acid, as shown in Figure 15. The obtained results confirm the positive influence of the carbonation pre-treatment in an autoclave at 175 $^{\circ}\text{C}$ and 71.5 bar on the leaching efficiency of nickel, magnesium and iron. An increase of the leaching efficiency from 25 to 40% for nickel was reached at 50 $^{\circ}\text{C}$ in the presence of carbonation pre-treatment. Similar effects were obtained for magnesium and iron under same conditions. A significant difference between leaching efficiency of nickel, magnesium and iron under previously mentioned conditions is not present.

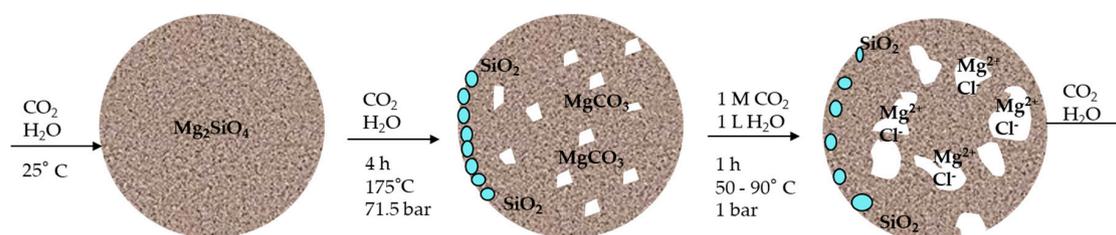


Figure 15. Mechanism of carbonation of olivine with a subsequent leaching with HCl.

The investigated leaching mechanism with carbonation as pre-treatment process, visualized in Figure 15, can be divided into four significant steps:

1. Injection of carbon dioxide and water in an autoclave with olivine and additives and a heating of the suspension to 175 $^{\circ}\text{C}$ in order to reach 71.5 bar.
2. Carbonation process at previously mentioned conditions in duration of 4 h.
3. Cooling of a water solution to an atmospheric pressure and temperature of 80 $^{\circ}\text{C}$.
4. Addition of hydrochloric acid and leaching of the carbonated product in duration of 1 h in the same way as for the untreated olivine.

All proposed steps should be performed in an autoclave with systems for on-line sampling and injection of hydrochloric acid at pressure.

Our fully developed process was presented at Figure 16.

In order to spare an added water (s/L: 0.1) enabling an enrichment of metals during new carbonation, obtained waste solution after filtration was again used in the autoclave, which is environmental friendly. The final solid residue will be sent to the cement industry.

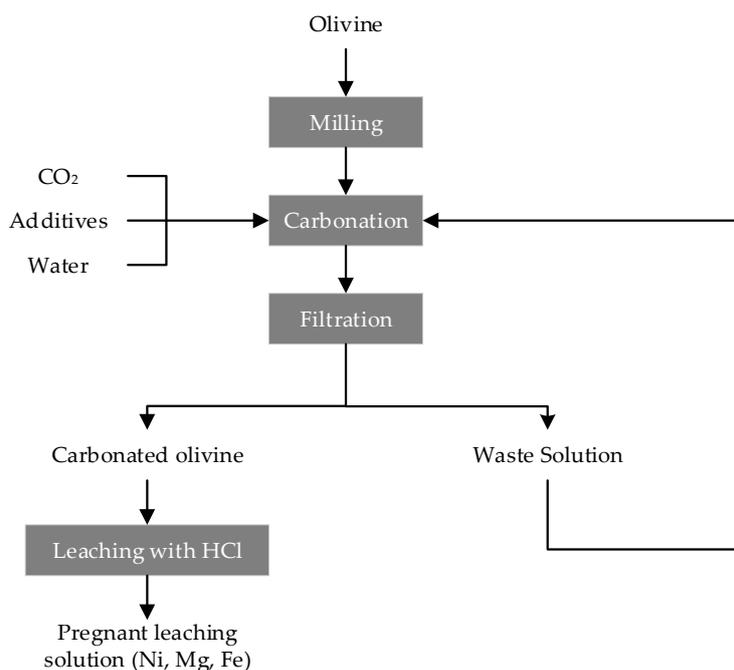


Figure 16. Recovery of nickel, magnesium and iron from olivine bearing ore during leaching with hydrochloric acid including a carbonation pre-treatment.

5. Conclusions

The results of the carbonation pre-treatment prior to leaching show that it is a promising and technically feasible step to increase a dissolution efficiency of nickel, magnesium and iron from olivine bearing ore. SEM analysis of the carbonated product at 175 °C and 71.5 bar has shown that magnesite crystals (2–5 µm) and very small particles of amorphous SiO₂ (100–200 nm) are formed as rhombohedrons or hexagonal prisms at the surface of partially carbonated magnesium silicate. A comparison of the leaching efficiencies at 50 °C of the investigated metals before carbonation and with carbonation confirms an increased leaching efficiency of nickel from 25 to 40%, which is also observed for magnesium and iron. An increase of temperature between 50 and 90 °C, a decrease of particle size from 150 to 20 µm and an increase of reaction time from 60 to 240 min leads to an increased leaching efficiency of nickel, magnesium and iron. A new mechanism of metal recovery during combined carbonation pre-treatment and a leaching offers an additional information about a behavior of nickel, magnesium and iron.

Author Contributions: C.M. performed the experimental work; S.S. conceptualized, 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.E. supervised the XRF, SEM and XRD-analyses and co-wrote the paper with R.T.; C.D. participated in our experimental part, analyzed the data and co-wrote the paper; B.F. supervised the personnel, provided funding and co-wrote the paper; P.K. conceptualized the research and helped in the discussion of the morphological characteristics of obtained magnesium carbonate and nanosilica. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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