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► To cite this version:

Laura Turri, Karine Gérardin, Hervé Muhr, François Lapticque, Alvaro Saravia, et al.. CO₂ sequestration by carbonation of olivine: a new process for optimal separation of the solids produced. *Green Processing and Synthesis*, 2019, 8 (1), pp.480-487. 10.1515/gps-2019-0016 . hal-03607634

HAL Id: hal-03607634

<https://hal.science/hal-03607634>

Submitted on 14 Mar 2022

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CO₂ sequestration by carbonation of olivine: a new process for optimal separation of the solids produced

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Abstract:

CO₂ sequestration by reaction with abundant, reactive minerals such as olivine has often been considered. The most straightforward, direct process consists in performing the reaction at high temperature and CO₂ pressure, in view to producing silica, magnesium and iron carbonates and recovering the traces of nickel and chromite contained in the feedstock mineral. Most of direct processes were found to have an overall cost far larger than the CO₂ removal tax, because of incomplete carbonation and insufficient properties of the reaction products. Similar conclusions could be drawn in a previous investigation with a tubular autoclave. An indirect process has been designed for high conversion of olivine and the production of separate, profitable products e.g. silica, carbonates, nickel salts, so that the overall process could be economically viable: the various steps of the process are described in the paper. Olivine particles (120 μm) can be converted at 81% with a low excess of acid within 3 hours at 95°C. The silica quantitatively recovered exhibits a BET area over 400 m² g⁻¹, allowing valuable applications to be considered. Besides, the low contents of nickel cations could be separated from the magnesium-rich solution by ion exchange with a very high selectivity.

Keywords:

CO₂ sequestration, olivine, products separation, carbonation, direct/indirect processes

1. Introduction

The increasing concentration of CO₂ in the atmosphere is attributed to the rising consumption of fossil fuels for energy generation or use around the world. In order to develop steel industry with low carbon dioxide emissions, chemical processes by reaction of CO₂ with minerals derived from silicate minerals, e.g. olivine can be considered [1, 2]. Because of their alkaline nature, silica-based minerals can react with acidic carbon dioxide at high pressure and temperature to generate carbonates and silica [3]. Various processes have been investigated as for instance in [4, 5]. However, the reaction has a significant cost, estimated in the range 80-200 € / tCO₂ depending on the process considered [3]. In this study, the recovery of the products has been considered in the global carbonation process, for an economic profitability and an environmental acceptability. More precisely, the conventional direct route for olivine carbonation has been compared to an indirect process currently under investigation and relying upon olivine acidic leaching followed by carbonation and separation stages. Comparison of the two processes is made in terms of reaction yields and quality of the products obtained.

2. Direct carbonation of olivine

2.1. Feedstock

The olivine used is produced in Norway and can be considered as a mixed Mg-Ni and Fe silicate. The main phase corresponds to the stoichiometry of Mg_{1,838}Fe_{0,156}Ni_{0,006}(SiO₄), with chromite particles present at approx. 0.38 wt.% and other inert minerals at trace levels. The particle size distribution of the GL30 ® grade used ranged from 70 to 250 µm with an average size of 120 µm (d(0.5) = 121 µm) to limit the grinding costs. More details about olivine characterization and properties are given in [6, 7].

2.2. Introduction to the direct process

Direct carbonation using olivine as feedstock has been considered as an alternative to convert CO₂ emissions into solid carbonates and silica. In this study, separation of carbonation products has been investigated for an environmental aspect and is specifically decisive for the economic viability of the process. The overall process of direct carbonation consists of the following steps (Figure 1):

- Olivine pretreatment has been considered before the carbonation reaction, due to the presence of impurities (Step 1). Two separation processes have been investigated successively: (i) flotation of chromite particles, for which the results are presented in [7], (ii) selective leaching of nickel which replaces magnesium in the forsterite matrix (Mg₂SiO₄) largely present in olivine.
- Direct carbonation of olivine particles (Step 2) is to be performed after separation of chromite and nickel. This step consists of two reactions, namely olivine dissolution then formation and precipitation of carbonation products. Both reactions can be conducted in the same reactor.
- Separation of the solids obtained by carbonation (Step 3). This step requires accurate characterization of the solids recovered after carbonation.

Examples of results obtained for the three steps are presented below, together with the potential and the limits of the direct process.

2.3. Pretreatment of olivine (Step 1)

Being both observed in olivine and in the carbonation products, chromite particles are not affected by high temperature carbonation. Various mechanical operations can be considered for the separation of chromite from olivine as magnetic or gravimetric separation [8, 9]. Flotation of chromite, based on surface phenomena, has been extensively investigated for the recovery of fine particles in the range 25-100 μm [10, 11]. In a previous study [7], flotation has been studied in a lab-scale column, using a sodium carbonate solution at pH 11 with cetyl trimethyl ammonium bromide (CTMAB). The enrichment ratio of chromite was found to be as large as 10 which demonstrated the potential of flotation for the recovery of chromite in a multistage flotation process [7].

Further, leaching of nickel for the pretreatment of olivine has been tested in view to purify the carbonation products. In various studies, dissolution of nickel contained in laterites (mixed iron and aluminium hydroxides and silicates) has been carried out using ammoniacal solutions [12, 13], as for example in the Caron process. In China, the recovery of nickel from serpentine by leaching in ammonium carbonate solution was studied downstream the mineral carbonation [14]. Selective separation of metals and ammonia recycling were also included in the process proposed.

In the present study, leaching tests of nickel have been carried out with 6 M ammonium hydrogencarbonate solution at 70 °C with three solids: GL30 olivine particles ($d(0.5) = 121 \mu\text{m}$), milled olivine ($d(0.5) = 25.5 \mu\text{m}$), and the solids formed by carbonation. In all tests, 5 g solids were treated in 100 mL ammoniacal solution under thorough stirring; three replicates were made for the three solids investigated. After leaching, the slurry has been separated by filtration; analysis of the liquid phase by ICP-OES yielded the dissolution yield of the various elements. As shown in Figure 2, the dissolution yield of nickel was only 5% for GL30 olivine, whereas it attained 80% with the milled olivine. Nickel contained in the carbonation products could be dissolved at less than 0.1%, which confirmed the fact that nickel should be separated from olivine before carbonation in the direct process. Moreover, Mg, Fe and Si were very little dissolved (dissolution rate below 3%) which clearly shows the high selectivity of the leaching process. However, in spite of the above results, this solution cannot be considered at pilot/industrial scale because of the energy required in the milling operation, in addition to the complex ammonia recycling loop [14] to be implemented.

2.4 Carbonation and products separation: potential and limits (Steps 2 and 3)

The reaction has been investigated in a pilot tubular autoclave, developed by Innovation Concepts B.V. [5, 15, 16]. The system consists of a stainless steel tube 1 m long and 47 mm inside diameter, submitted to sudden rocking at regular intervals. The olivine used here was the pristine mineral, i.e. not treated by flotation. Carbonation tests have been carried out during 90 min, at 175 °C and 100 bars with CO_2 , plus N_2 as pressure driving gas. 600 g olivine were added to 1200 cm^3 solution of 0.64 M sodium hydrogencarbonate, 0.5 M oxalic acid and 0.01 M ascorbic acid. The effects of the operating conditions presented in [5, 6]. have been evaluated on the carbonation yield.

The conversion yield of olivine has been estimated by thermogravimetric analysis (TGA), from the thermal decomposition of carbonates in the range 400 - 600 °C. Total weight loss in TGA for a completely converted (carbonated) olivine was calculated at 37 % taking into account its equivalent stoichiometry given above. Previous results [6] have shown the limited carbonation because of

inhibition phenomena of the reacting surface [5, 6]. Conversion of GL30 olivine was found to slightly increase with time, up to 30 % after 10 hour-long carbonation. The conversion also increased with the decrease in particle size, passing from 10 % for GL 30 particles (120 μm) after 90 min. to 60 % with 4 μm particles. However, in this case, the energy required for grinding increases from 58 kWh/t \approx 3.1 €/t (120 μm) to 210 kWh/t \approx 11.3 €/t (4 μm), which can hardly be considered at industrial scale.

The formation of a passivation layer has been evidenced on the surface of the unreacted olivine by SEM, EDX and DRX, as presented in [5, 6]. This layer is mainly formed by a silica-based mineral, and considered as the limiting factor, leading to insufficient dissolution yield of particles over 10-20 μm as reported in most relevant papers.

The solids obtained after Step 2 were shown to consist in a fine particles fraction below 106 μm and a coarser (residue) fraction [6]. The residue is principally formed by unreacted olivine, whereas the fine particles consist mainly of mixed Mg-Fe carbonates (mainly below 40 μm) and silica (over 40 μm): this segregation with particle size appears favourable for the separation of carbonation products. Nevertheless, the presence of coprecipitated particles of carbonate-silica also revealed by microscopic analysis, is to affect the efficiency of the separation operation.

The BET area of the fine particles fraction was shown to be a decreasing fraction of the carbonate fraction in this solid phase (Figure 3) with all the data obtained with various operating conditions. The BET area of very rich carbonate fractions was as low as 2,3 m^2/g , a value far below the minimum level at 15 m^2/g , recommended for applications in concrete [17]. Conversely, the values reached 35 m^2/g for carbonation tests, with carbonate fractions lower than 60% in the fine particles. However, in this case, the products also included a significant fraction of unreacted olivine, corresponding to poorly efficient separation of the solids obtained by carbonation.

Although of fundamental interest, the results obtained by direct carbonation exclude any possible benefit from CO_2 sequestration, mainly because of insufficient dissolution yields [6] and insufficient quality of the reaction products in terms of purity and surface area.

3. Indirect carbonation of olivine

3.1. Description of the overall indirect process

Indirect process can be considered as an alternative to the potential limits of direct carbonation which consists of the sequence of olivine dissolution by reaction with acidic solutions, followed by a series of separation and reaction steps [1]. For this purpose, an overall indirect route is currently investigated by the authoring teams for the production of highly valuable minerals, with the aim of profitable CO_2 sequestration using reactive silicates. The presence of chromium- and nickel-based minerals can be valuable upon their efficient separation, but a potential hazard source otherwise. The overall process designed with the same olivine feedstock, consists of the following steps after the separation of chromite particles by flotation (Figure 4):

- Olivine particles are dissolved in a concentrated acidic solution (WP1), yielding an acidic solution of divalent magnesium, iron and nickel cations, and solid amorphous silica [18-20] which is gradually formed as the acid is consumed by the dissolution. Care had to be taken for a nearly complete dissolution with a minimum excess of acid and the recovery of concentrated metal cation

solutions. The preparative formation of microporous silica particles with a high BET area has also been investigated in view to possible use in paper industry, tyre manufacturing or even as sorbent of inkjet paper.

- First separation step of metal cations (WP2): the low contents of nickel have to be separated from the metal salt solution. In spite of the large fluxes of liquid solution to be treated, ion-exchange (IEX) technique has been selected because of existing, reliable technology and specific resins. Besides, the use of resins is also free from inherent drawbacks of solvent extraction processes or reactants use leading to subsequent pollution of the separated metal solution [21].
- Selective carbonation and final separation of metal species (WP3). The slightly acidic solutions resulting from WP1 and WP2 have to be gradually neutralized by addition of slags acting as low-cost alkaline materials. The mixed Mg-Fe can be carbonated at approx. 200°C and under 20 bars CO₂. However, two-stage process at two different pH levels is required for optimal separation, with intermediate addition of slag for pH increase.

Evaluation of technical and financial viability of the overall process, together with its integration in industrial areas have finally to be investigated. Examples of results obtained for WP1 (olivine dissolution and silica recovery) and WP2 (metal separation by ion exchange) are illustrated below.

3.2. Olivine dissolution in acid and silica recovery (WP1)

A literature survey has shown that olivine, in the form of a suspension of 10-100 µm, could be dissolved in a solution of hydrochloric or sulfuric acid at concentrations near 3 M, for temperatures ranging from 60 to 100 °C [22, 23]. Moreover, precipitation of silica in acidic media has been the subject of a number of studies [18-20], from which the experimental protocol could be defined.

Dissolution was extensively investigated in stirred vessels, with a volume of 250 mL (lab scale) or 1 L (pilot). Discontinuous tests have been made in 3 M sulfuric acid, under inert atmosphere to avoid undesired oxidation of divalent iron species, at solid-over-liquid (S/L) weight ratio varying from 80 to 180 g/L. Dissolution is nearly complete within a few hours, in agreement with formerly reported works [17-19]. Then, silica is formed in the reaction vessel by neutralization with NaOH, for pH in the range 1-2. Two fractions of solids have been recovered from the leaching reactor: the upper, lighter fraction corresponds mainly to silica, whereas the solids settled in the vessel (bottom fraction) contains also unreacted olivine [24].

As shown in Table 1, operation at 95°C with 20% of sulfuric acid excess allowed to obtain a conversion rate of 93% within 3 hours. Silica nanoparticles (upper fraction) with a BET area near 500 m²/g have been recovered quantitatively which is promising for the future beneficiation of solids. After optimization of the lab scale dissolution, low excess of acid (12%) at 95°C, with 180 g/L olivine and a short reaction time (90 min) have been tested, with a conversion rate of 81%. In order to evaluate the potential of the process, dissolution of olivine has also been conducted in the larger stirred vessel for 3 hours, under comparable conditions: olivine conversion attained 81% as shown by both analysis of the solid formed, and analysis of the concentrated resulting liquid phase to evaluate the mass balances in metal cations. For the three tests presented here BET area higher than 400 m²/gr has been found for the upper fraction which is promising for silica beneficiation [24].

3.3. First separation of metal cations by ion-exchange (WP2)

In the indirect route of carbonation process, the low contents of nickel have to be removed from the olivine leachate. For this purpose, separation by IEX has been studied. Several commercial resins have been screened for the separation of Ni^{2+} in an acidic solution. Chelating resins with the iminodiacetate functional group were reported to allow selective adsorption of nickel from tailings of pressure acid leaching plants but for pH of the feed solution near 4 or 5 [25]. In contrast, Dowex M-4195® resin can form complexes with transition metals in acidic solutions through their free electron pair-bearing nitrogen atom (bis-picolylamine group) [26, 27]. Separation of nickel from sulfate or chloride solutions with this resin at pH below 3 was reported [26, 28].

In this study, separation tests of nickel by IEX have been conducted with Dowex M-4195® resin, in a 150 mm long column being 15 mm in diameter and with a bed volume (BV) at 21 cm^3 . The resin was conditioned according to the recommendations of the manufacturer, by washing with deionized water and 1 M sulfuric acid to remove the impurities from the resin and to obtain a free base form. The feed solutions were injected in counter-current flow, using a peristaltic pump at 1 mL/min, i.e. nearly 3 BV/h. 64BV were run for the loading tests. ICP-OES analysis of the collected liquid fractions allowed the adsorption kinetics of Mg, Fe, Ni cations to be evaluated.

First, pure nickel solutions (5,87 g/L Ni) with various pH have been prepared to evaluate the capacity of the resin (Table 2). All tests have been conducted until saturation of the resin. For $\text{pH} > 1.5$, the capacity was in the range 0.81-0.89 eq/L, whereas it decreased to 0.48 eq/L at pH 1, in accordance with the literature [26].

Feed solutions have been prepared with 0.025 g/L Ni, 0.5 g/L Fe, 2.7 g/L Mg: the respective proportions of metal cations are in accordance with those in the liquid phase to be issued from olivine dissolution. As expected, the adsorption of nickel cations on the resin was found to depend on the solution pH (Figure 5). After injection of the feed solution, the ratio of the nickel outlet concentration over the concentration of the feed solution (C/C_0) was measured at 0, 0.19 and 0.61 after 64 BV, respectively at pH 2, 1.5 and 1. The results also confirmed the performances of the resin for a pH larger or equal to 1.5.

In the present work, both adsorption (loading) and desorption (elution) have been investigated. Before nickel desorption, a backwash with 1.5 BV of deionized water through the column was conducted to remove impurities as Fe and Mg cations. One-molar sulfuric solution was then injected to recover Ni cations in the elution step. At pH 1.5 of the feed solution, the ratio C/C_0 of nickel reached 30 after 1.5 BV with 1 M sulfuric acid (Figure 6). This value also expresses the enrichment factor of the eluate in comparison to the acidic solution to be treated. Mg and Fe were not detected after the backwash; moreover, the ratio C/C_0 for Ni near 1 observed during the backwash corresponds to the dead volume. These results confirmed the selectivity of the resin for nickel separation from the Mg-Fe solution.

The global yield of the various tests differing from the solution pH is presented in Table 3. For $\text{pH} < 1$, less than 60 % of nickel could be separated. At pH 2, more than 90 % of nickel was recovered in the sulfuric eluate, however with 0.4 % of Fe^{2+} contained in the feed solution. Suitable conditions have been found for both nickel adsorption and production of single Ni solution at pH 1.5. This shows the potential of IEX for low concentrations of Ni cations. After the removal of Ni ions from the liquor solution, the Mg-Fe solution can either be driven to the carbonation stage or undergo a second IEX

stage for the separation of iron species. However, because of the far larger content of Fe^{2+} , iron carbonation should be preferred.

The comparison between the two carbonation routes is summarized in Table 4. Although the direct process is of an easier implementation, the carbonation rate was limited by the passivation of the olivine surface. Moreover, the separation of carbonation products was limited by their coprecipitation. The indirect carbonation can allow high dissolution yields and leads to highly valuable silica, nickel salts, and separate iron and magnesium carbonates.

4. Conclusion and further prospects

The possible reconciliation of reduction of CO_2 emissions by its sequestration and the development of green processes for the production of valuable products has been considered in this study. We propose here an alternative to the conventional direct carbonation of olivine by an original process, whose various steps are still under investigation and development. Although some parts of the indirect route have to be validated e.g. iron and magnesium carbonations, the potential of the overall indirect process was demonstrated for the quantitative production of nanostructured silica and concentrated solutions of metal cations. Ion-exchange technique has been shown promising for the separation of low concentration Ni cations. For both tasks, the targets defined could be attained.

After experimental investigation of the carbonation step of divalent Fe and Mg cations, the overall process will be evaluated in terms of energy demand and costs. Life cycle analysis has also to be conducted for assessment of its technical and environmental validity.

Acknowledgments

The study is a part of VALORCO project, coordinated by ArcelorMittal and funded by ADEME, to develop a steel industry with highly reduced carbon dioxide emissions. Thanks are also due to French Ministry of Research and Region Lorraine for co-funding most of the facilities used here, within the project "Sustainable Chemistry and Processes" (CPER Lorraine).

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Table 1. Operating conditions and dissolution yield (X_{diss}) of olivine.

Parameters	S/L ratio (g/L)	Acid excess (%)	Time (min)	% X_{diss}	% SiO ₂ : Upper	% SiO ₂ : Bottom	BET (m ² /g): Upper
Lab scale	80	20	180	93%	96%	56%	> 500
Lab scale Optimization	180	12	90	70%	87%	20%	400
Pilot	100			81%	93%	23%	440

Table 2. Capacity of the resin depending on solution pH, with a 5.87 g/L Ni solution

Solution pH	1	1.5	2	4
Resin capacity (eq./L)	0.48	0.81	0.86	0.89

Table 3. Overall yield of ion exchange depending on solution pH, using 25 ppm Ni, 2.7 g/L Mg, 0.5 g/L Fe.

Over. yield %	pH 0.55	pH 0.85	pH 1	pH 1.5	pH 2
Fe	0.0	0.0	0.0	0.0	0.4
Mg	0.0	0.0	0.0	0.0	0.0
Ni	22.5	42.4	59.1	85.3	93.1

Table 4. Comparison between direct and indirect carbonation routes

Carbonation	Direct process	Indirect process
Advantages	<ul style="list-style-type: none"> - Carbonation reaction in one step - Easy to implement 	<ul style="list-style-type: none"> - Provide a high dissolution rate - Production of high value added silica - Control of the operating conditions - Selective carbonation - Higher carbonation rate - Improvement of the products separation
Drawbacks	<ul style="list-style-type: none"> - Limited Carbonation yield - Passivation layer on olivine - Coprecipitation of products 	<ul style="list-style-type: none"> - Requires several unit operations

Figure

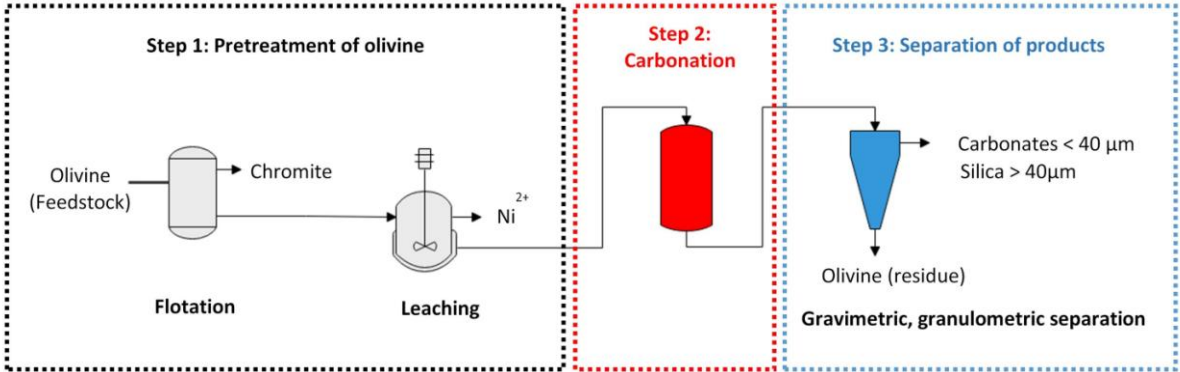


Figure 1. Schematic view of the process for CO₂ sequestration by direct carbonation of olivine.

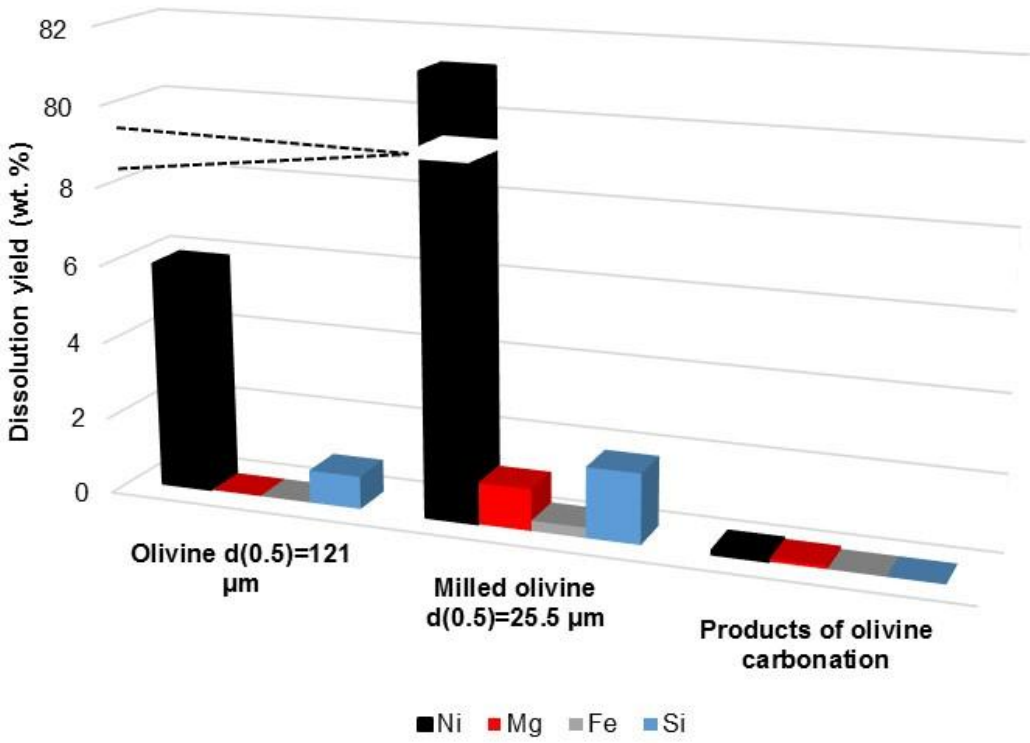


Figure 2. Dissolution yield of olivine and carbonation products using ammonia solution.

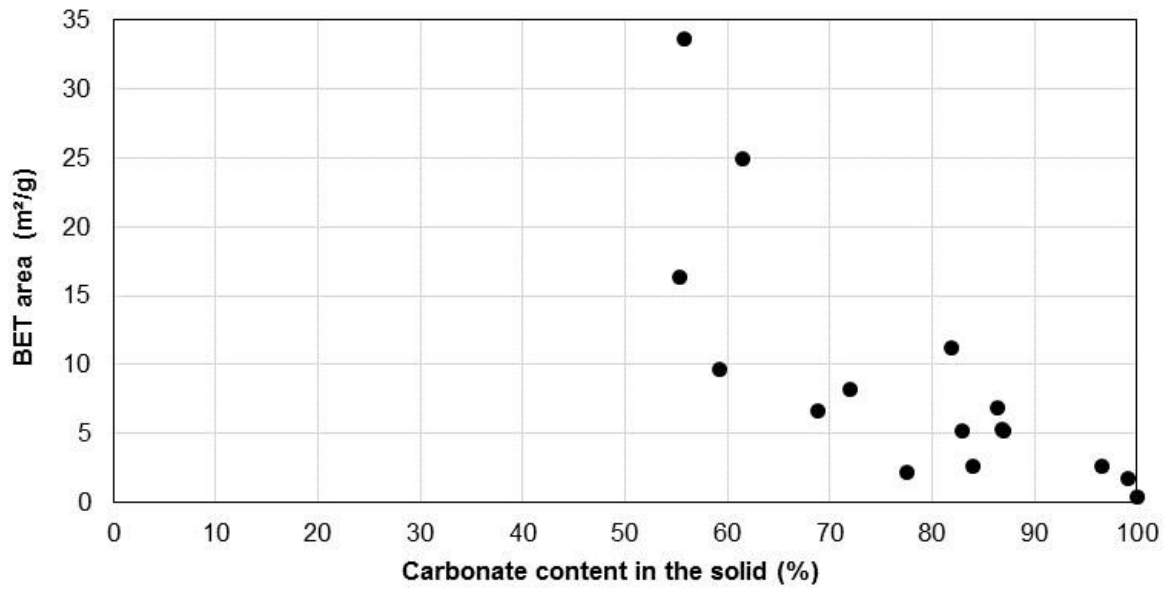


Figure 3. BET area vs. and carbonate content in the fine particles for various operating conditions.

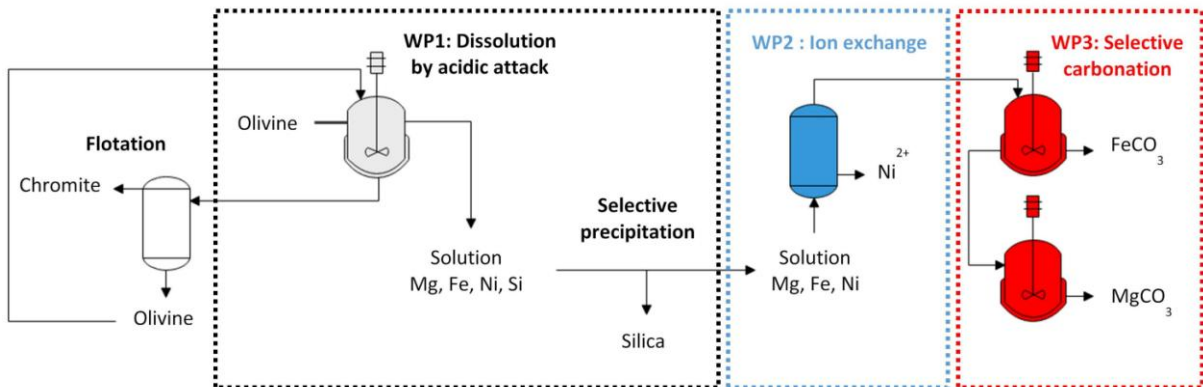


Figure 4. Schematic view of the process for CO₂ sequestration by indirect carbonation of olivine.

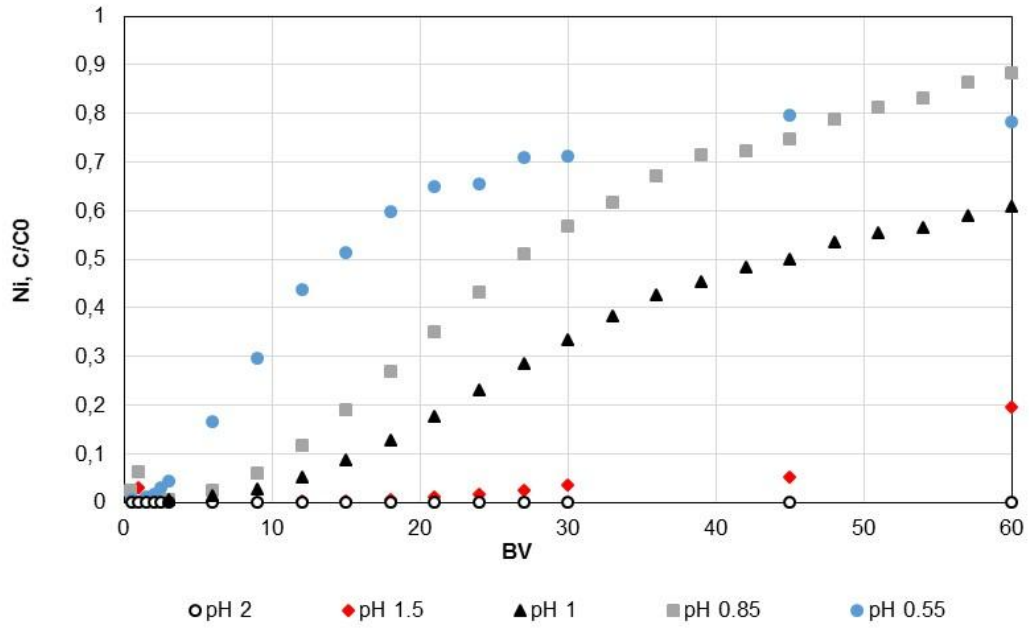


Figure 5. Adsorption of nickel depending on pH of 25 ppm Ni, 2.7 g/L Mg, 0.5 g/L Fe solutions

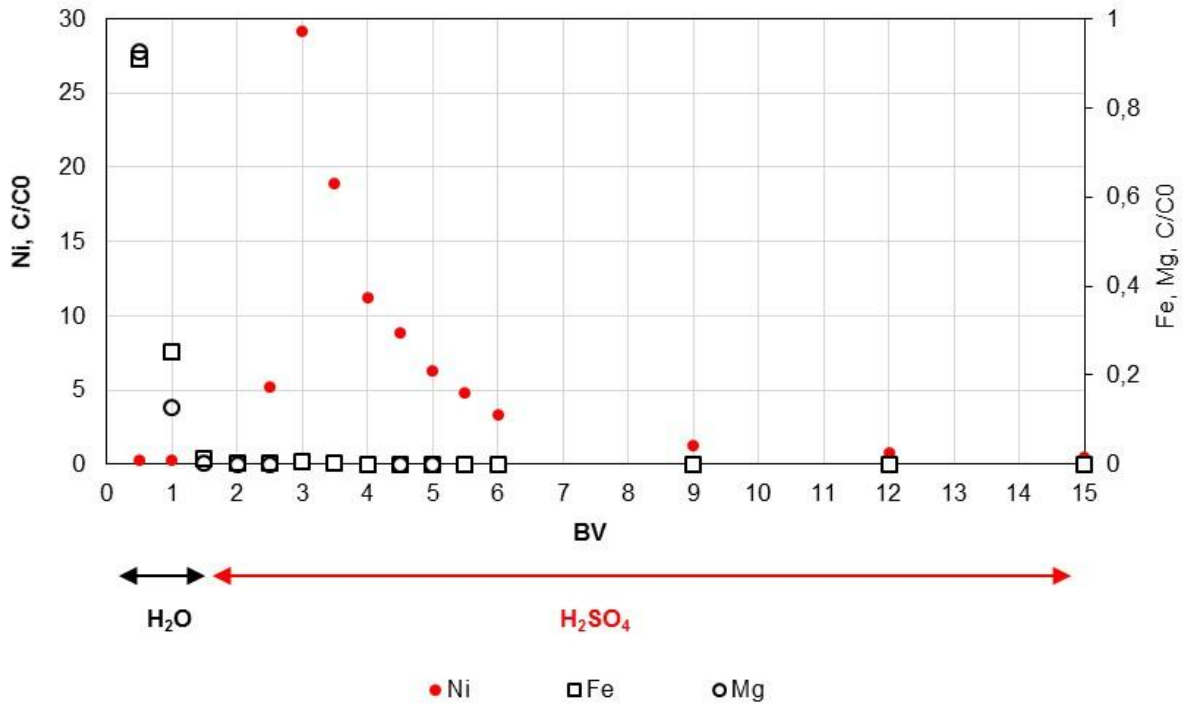


Figure 6. Elution of nickel for solution containing 25 ppm Ni, 2.7 g/L Mg, 0.5 g/L Fe at pH 1.5