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Original scientific papers

Carbonation of minerals and slags under high pressure in an autoclave

Карбонизация минералов и шлаков под высоким давлением в автоклаве

Везивање угљен-диоксида са минералима и шљаком при високом притиску у аутоклаву

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ABSTRACT:

Introduction/purpose: Carbonation of minerals (olivine and wollastonite) and secondary materials such as slag under high pressure in autoclaves has high importance due to environmetal problems.
Methods: The most important for this process is to have a good knowledge of the behavior of carbon dioxide in water solution under high pressure, the precipitation of silica, dissolution of metals such as nickel and magnesium as well as subsequent filtration.
Results: The carbonation process of olivine und slag under high pressure (from 40 to 80 bar) in an autoclave was successfully performed at 175°C, with and without additives.
Conclusion: A comparative analysis has confirmed better carbonation of slag (max. 300 kg/ton) in comparison to that of olivine (max. 70 kg/ton) under the same conditions.

KEYWORDS: carbonation, olivine, slag, autoclave, additives.

Резюме:

Введение/цель: Карбонизация минералов (оливина и волластонита) и вторичных материалов под высоким давлением в автоклавах очень важно для охраны окружающей среды.
Методы: Наиболее важным в данном процессе является познание того, как себя ведет диоксид углерода в водном растворе под высоким давлением, как происходит растворение металлов таких как никель и магний, а также их последующая фильтрация.

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Результаты: Процесс карбонизации оливина и шлака под высоким давлением (от 40 до 80 бар) был успешно проведен при 175 °C в автоклаве с добавками и без них.

Выводы: Сравнительный анализ показал, что карбонизация шлака (макс. 300 кг / т) по сравнению с карбонизацией оливина (макс.70 кг/ т) в одинаковых условиях производится намного лучше.

Ключевые слова: карбонизация, оливин, шлак, автоклав, добавки.

Abstract:

Увод/циљ: Везивање угљен-диоксида са минералима (оливин и воластонит) и секундарним материјалима при високом притиску у аутоклаву врло је важно за заштиту животне средине.

Методе: За овај процес најважније је понашање угљен-диоксида у воденом раствору при високом притиску и растварање метала као што су никал и магнезијум, као и наредна филтрација.

Резултати: Процес везивања угљен-диоксида са оливином и шљаком успешно је изведен у аутоклаву на 175°C између 40 и 80 бара у присуству и одсуству адитива.

Закључак: Упоредна анализа је потврдила боље везивање угљен-диоксида са шљаком (максимално 300 kg/t) у поређењу са оливином (максимално 70 kg/t) при истим условима.

Keywords: везивање угљен-диоксида, оливин, шљака, аутоклав, додаци.

Introduction

Carbon dioxide has the fourth highest presence in Earth's atmosphere after nitrogen, oxygen and argon and plays a significant role in global warming due to the greenhouse effect. Because of the significant increase of CO_2 emissions, carbonation is a promising process in which carbon oxide reacts with compounds with high metal oxide compositions to form chemically stable and insoluble metal carbonates. The choice of experimental parameters (temperature, pressure, solid/liquid ratio, mixing rate, time) for carbonation in an autoclave is of high importance. Although it is reported in literature (Gadikota et al, 2014, pp.4679-4693) that a higher temperature favors mineral dissolution and carbonation, there exists an optimum level of a temperature range. The carbon dioxide solubility is reduced if the temperature is too high. On the other hand, low temperature slows mineral dissolution. The authors suggested that higher conversion was achieved with higher temperature but with a limit to 185°C. They performed an olivine experiment with varied temperatures at partial pressure of 141 bar, for 3 hours with an additive of 1.0M NaCl + 0.64 $NaHCO_3$ with 15 wt% solid, and at a stirring speed of 800 rpm. The final carbonation rates at 90, 125, 150, and 185°C were found to be 3.0, 28.2, 70.5 and 85.3%, rspectively. An increase in reaction time from 3 hours to 5 hours does not influence the carbonation efficiency.

The slag carbonation between 40°C to 160°C with partial pressure set at 48 bar and a reaction time of 1 hour (Chang et al, 2011) confirmed that conversion increased with increasing temperature because of a higher carbonation rate of calcium at higher temperatures. In this experiment, blended hydraulic cement BHC slag showed a more unique route because this conversion decreased after the temperature had exceeded 100°C. It could be caused by the reduction of carbon dioxide dissolution as reaction temperature increased.

It is expected that higher olivine to carbonate conversion is achieved with increased pressure of carbon dioxide (Santos et al, 2016, pp.1-6). From his experiment, the conversion rate is almost doubled (from 8% to 16%) when the total pressure was doubled from 60 to 120 bar after 3 hours of reaction time. The reason behind it was that a higher carbonic acid concentration improved mineral dissolution and, at the same time, promoted carbonate precipitation.

The liquid to solid ratio L/S represents the weight ratio of water to solid in aqueous carbonation slurry. The optimal proposed L/S ratio was 10 mL/g (Rahmani et al, 2014, pp.5953-5958). Although a high L/S ratio was advantageous for decreasing water treatment and saving energy during dehydration, additional water is required to extract calcium and magnesium in the indirect carbonation process. The reduction of the

L/S ratio also has small contribution to the overall conversion rate, which suggested it could result in more calcium and magnesium ions in the solution and, therefore, stronger ionic strength.

As the L/S ratio increased, the carbonation rate also increased because aqueous carbonation was dominant (Chang et al, 2012, pp.97-106). As the L/S increased more, however, the conversions did not increase because the excess amount of the aqueous medium formed a mass transfer barrier, and, as a result, the ionic strength was lower. There was a limit to the liquid to solid ratio between 10-20 mL/g for the carbonation process because a large amount of water could limit the conversion rate. Dunite carbonation in a batch-tubular reactor was performed with an increased S/L ratio of 2.8 g/ml (Agrawal & Mehra, 2020). The results revealed the precipitation of magnesite under diffusion limited conditions. The SiO. formation and magnesite precipitation fill the pore space and the fractured zone on the rock surface.

The positive role of the added $NaHCO_3$ in olivine carbonation was confirmed, but not investigated in detail (Stopic et al, 2018, pp.193-207). The synthesis of magnesium carbonate was studied using olivine under a partial pressure of carbon dioxide higher than 100 bar at 175°C. The combination of organic acids such as oxalic acid and ascorbic acid accelerates the carbonation of olivine, reducing the formation of the silicate passive layer (Stopic et al, 2019, pp.135-147). The synthesis of nanosilica was studied via olivine carbonation using the size fraction between 20 and 63 µm with the solid/liquid ratios of 1:10 at 175 °C and a partial pressure of CO_2 higher than 100 bar in an autoclave in the presence of additives such as sodium bicarbonate, and oxalic and ascorbic acid. Under the above-mentioned conditions, ideally spherical particles of silica below 500 nm with amorphous grains were produced during carbonation. An increase in stirring speed from 600 rpm to 1800 rpm in an autoclave leads to the increased formation of magnesium carbonate and silica. An increased stirring speed has a positive influence on the separation of the formed silica-rich layer of the non-reacted magnesium silicate. On the other hand, the pressure in an autoclave was increased from 120 to 170 bar with an increasing stirring speed from 600 to 1800 rpm, which is an additional support for the silica separation and precipitation from the solution. The use of strong turbulence for better mixing of reactants to avoid the formation of a silica passivation layer was mostly studied in literature (Stockmann et al, 2014, pp.31439-31445). Using a strong mixing device, such as a high gravity rotary reactor, might also help to resolve this issue.

A new mechanism model for metal extraction (nickel, iron, magnesium) from olivine-bearing ore by avoiding silica gel formation during leaching with hydrochloric acid including a carbonation pre-treatment was proposed (Matus et al, 2020, pp.811-827). This study explains additionally the behavior of metals such as nickel, magnesium, and iron during the carbonation of olivine-bearing ore and the leaching of a carbonated solid product.

In accordance with the previously mentioned analysis of the reaction parameters, an experiment was designed in order to reach maximum carbonation efficiency. This paper will explain the carbonation of olivine and the carbonation of slag under chosen experimental conditions. A comparison of their carbonation efficiencies will be mentioned in order to choose the most suitable material for scale up experiments.

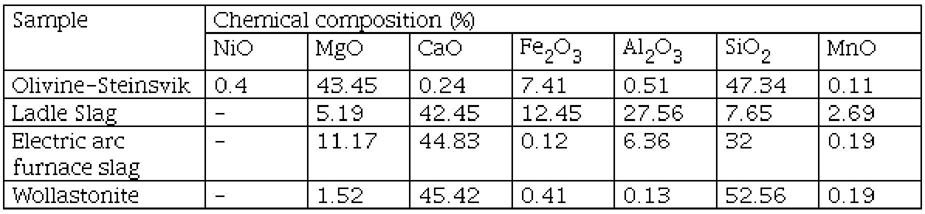
EXPERIMENTAL

Material

The samples of olivine (Norway), ladle slag, and electric arc furnace slag (Germany) were studied for carbonation in water solution under high pressure conditions in an autoclave. It should be noted that, despite different particle sizes, the results of the XRF analysis are very similar in the case of different olivine Steinsvik. The characterization was performed by the X-ray fluorescence (XRF) technique, type PW2404 (Malvern

PANalytical, Malvern, UK). Milling was performed using a Roller Mill, Type LWBP 2/2 (Karl Merz Maschinenfabrik GmbH, 1972 (year of manufacture), Heschingen, Germany). Sieving was performed using a Sieving Maschine, Type Prüf 86 (Siebtechnik GmbH, Mühlheim an der Ruhr, Germany). In the case of slag, all tests were run with a particle size < 63 µm, since a slag particle size analysis was not part of this work. The presence of calcium oxide and magnesium oxide is the most important parameter for the carbonation process. Because of different behaviors of metal silicate and metal oxide through carbonation, the mineralogical composition mostly influences high carbonation efficiency. The maximum content of calcium oxide and magnesium oxide in electric arc furnace (EAF) slag amounts to 55.90%, in contrast to its minimum presence found in mineral olivine (43.67 %). Because of this situation, the maximum carbonation value was expected for EAF and the minimum carbonation value for olivine. Besides the chemical compositions of the studied samples, the particle size and the active surface area have an important role in a higher carbonation level. A higher amount of silicon in the sample can be later included in a newly formed passive layer as a barrier for the carbonation process in an autoclave. Some part of iron can also be carbonated. Aluminium and manganese are not included in the carbonation process.

TABLE 1
Chemical compositions of the samples used in the carbonation process



Sample	Chemical composition (%)						
	NiO	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	MnO
Olivine-Steinsvik	0.4	43.45	0.24	7.41	0.51	47.34	0.11
Ladle Slag	-	5.19	42.45	12.45	27.56	7.65	2.69
Electric arc furnace slag	-	11.17	44.83	0.12	6.36	32	0.19
Wollastonite	-	1.52	45.42	0.41	0.13	52.56	0.19

The used samples are shown in Figure 1:

Olivine, Norway

Ladle slag, Germany

Electric arc furnace slag, Germany

FIGURE 1
The used samples in the carbonation process

Procedure

The treatment of olivine first included the operations such as milling, sieving, and carbonation under high pressure conditions with an additional filtration and a chemical analysis of solid and liquid. The carbonation tests were carried out in a 9.9 L autoclave (Hastelloy C22 pressure reactor) of a kiloclave Type 3E (Büchi, Switzerland) with electric heating and water cooling (as shown in Figure 2) at $175^{\#}$C with 71.5 bar pure grade CO_2 in the presence of additives such as sodium bicarbonate, oxalic acid, and ascorbic acid. The planned experiments in this work will show how the the previously mentioned results from the experiments performed in the 0.25 L and 1.0 L autoclave relate to the 10 L autoclave experiment and validate the obtained results.

FIGURE 2
Autoclave for the carbonation process

For the carbonation of samples, the stabilization initial pressure is of great importance. The stabilization pressure is the pressure set at the beginning of the experiment by CO_2 injection. This pressure was set at room temperature. The adjustment was made by continuously adding gas until the pressure stabilized in the system. Since there is reduction in the pressure in the system during gas introduction due to the chemical reaction of CO_2 with water, it is important to perform stabilization. In this regard, it was observed that the higher the stabilization, the higher carbonation levels were obtained. However, this also depended on the grain size and the returned liquid. The Büchi software, Switzerland, was used for the analysis of pressure, temperature, and stirring speed in an autoclave.

Reaction parameters

In the carbonation tests, the increase of the carbonation degree by changing the influencing parameters was investigated. Some parameters were kept constant as they were found to be suitable according to the previously mentioned literature. In the case of the tests with olivine ore, the solid/liquid ratio and the stirring speed were kept constant.

The following listed carbonation parameters are shown in Table 2.

TABLE 2
List of the reaction parameters (Additives: 0.64 M sodium bicarbonate, 0.04 M oxalic acid & 0.01M ascorbic acid, 600 rpm, solid/Liquid= 1 kg/8L)

Material	Particle size (µm)	Initial stabilizing pressure (bar)	Max. Pressure (bar)	Time (hours)	Temperature (°C)
Olivine	<11, <20, 20-63, <63	15-30	40-80	2-4	100, 175
Ladle Slag, EAF-slag, wollastonite	<63	15-20	50	4	100, 175

By calculating the degree of carbonation, it is possible to determine the maximum CO_2 absorption capacity of the feedstock. It must be taken into account that not all of the studied material is capable of absorbing CO_2. Therefore, only the proportion of MgO is considered for olivine and the proportion of MgO and CaO for slag. The loss on ignition gives a global estimate of the experiment efficiency, since the higher the loss on ignition, the more CO_2 was absorbed in percentage terms.

The particle size plays a decisive role in the success of olivine carbonation. The smaller the particle size, the higher the degree of carbonation achieved (as shown in Figure 3). The carbonation reaction of magnesium silicate from olivine was presented with Equation 1:

$$Mg_2SiO_4 + 2\ CO_2 \rightarrow 2\ MgCO_3 + SiO_2 \tag{1}$$

An increase in pressure of carbon dioxide increases carbonation efficiency. The maximum carbonation efficiency of olivine at 175 °C amounts to 70 kg CO_2/ton.

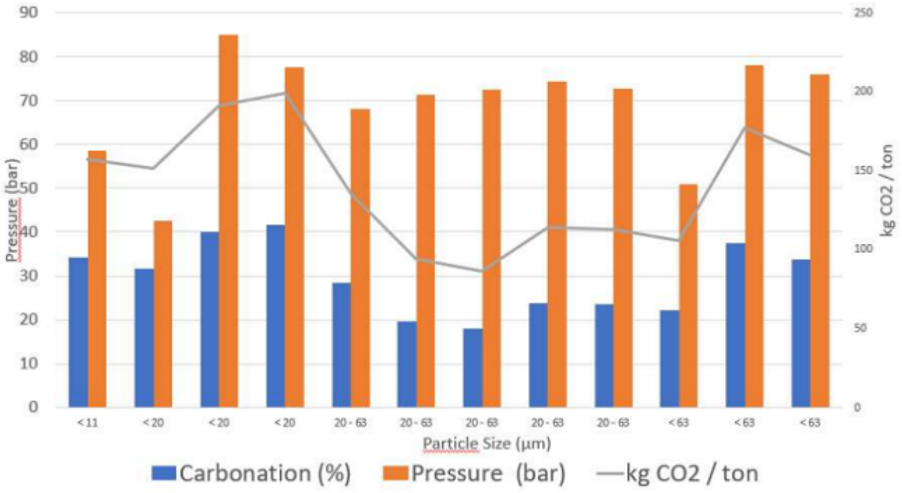


FIGURE 3
Degrees of carbonation for different particle sizes of olivine in the presence of additives at 175°C, 600 rpm, S/L=1/8

The result of the test with a decreased particle size smaller than 11 µm is different from the expected value. Here, the carbonation degree was 34.28% despite an extremely small particle size. This raises a possibility that there is a critical particle size between 0-20µm above which further grinding of olivine is no longer worthwhile. The carbonation of slags and wollastonite was performed in the presence and absence of additives, as shown in Figure 4.

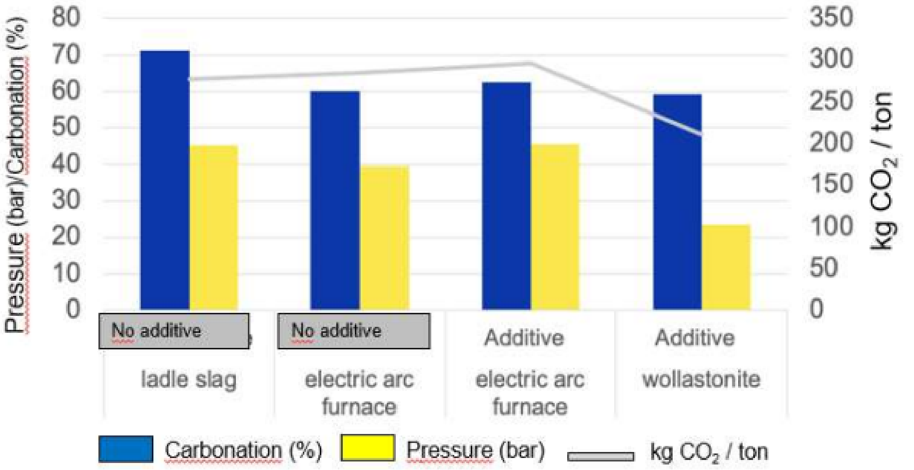


FIGURE 4
Degrees of carbonation for different types of slags at 175°C, 600 rpm, S/L=1/8

After a confirmation that EAF slag is suitable for carbonation, it was investigated whether the addition of additives affects the degree of carbonation. As shown in Figure 4, the carbonation degree of EAF slag both without additives and in the presence of additives amounts to 60.13%, which confirms no influence and significance of their using in slag carbonation. This result was confirmed in the case of wollastonite carbonation.

$$CaSiO_3 + CO_2 = CaCO_3 + SiO_2 \tag{2}$$

The maximum carbonation efficiency was obtained for ladle slag (about 70 % or 300 kg CO_2/ton) at 175 °C in the absence of additives. However, only one test was run with this slag because solids cemented to the bottom of the reactor and the cleaning of the reactor was very difficult. To free the carbonated ladle slag from the reactor, a two-hour leaching process at 100°C with acetic acid was necessary.

In the case of electric arc furnace slag (EAF slag), the degree of carbonation is somewhat lower than for ladle slag. However, no cementation problems were encountered with EAF slag, making this slag suitable for the carbonation test. The disadvantage of EAF slag is the formation of small stones during the carbonation tests. This caused some problems during the subsequent filtration process.

CONCLUSION

Carbonation of minerals and slag in an autoclave seems to be a prominent solution to the problem of rising carbon dioxide levels in the air. Carbonation of olivine and slag was successfully performed at 175°C under high pressure conditions (40-80 bar) in a 10 L autoclave. A comparative analysis has confirmed better carbonation of slag (max. 300 kg CO_2/ton) in comparison to that of olivine (max. 70 kg CO_2/ton) under the same conditions. The presence of additives such as sodium bicarbonate and oxalic and ascorbic acid is very important for olivine carbonation, but without influence in the case of slag, which is very important regarding an efficient cost-effectiveness analysis.

One challenge of mineral carbonation is to make it economically feasible. The obtained results will help to design future mineral carbonation experiments in scale up conditions.

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