

A POSSIBLE WAY TO STORAGE CARBON DIOXIDE ON MECHANICALLY ACTIVATED OLIVINE (Mg,Fe)₂SiO₄

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Abstract

This paper deals with mechanical carbonation of olivine by dry and wet modes. Mechanical activation and carbonation of the olivine samples have been performed using a planetary mill, Pulverisette 6 (Fritsch, Germany). A series of experiments were produced where the activated products were exposed to carbon dioxide during activation in presence of water and by dry mode of milling. To identify mechanically induced changes in surface of the mineral, specific surface area measurements have been used. To identify carbon dioxide sequestration, infrared spectroscopy and determination of total carbon have been used. Infrared spectroscopy seemed to be a suitable method for characterization of CO₂ absorption on mechanically modified olivine.

Introduction

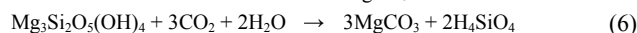
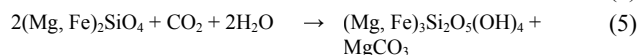
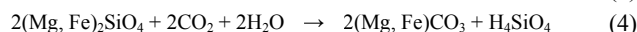
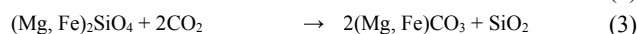
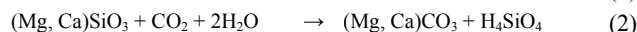
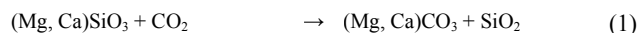
Global warming is an important environmental issue which is rapidly becoming a part of popular culture. In the history of civilizations, the 20th century can be characterized as a century of explosive growth in energy consumption and rapid increase in population worldwide, along with unprecedented pace of inventions of new technologies and ever-increasing expansion of man-made materials. The enhancement of the natural greenhouse effect is caused by emissions associated with human activities of greenhouse gases such as carbon dioxide, methane, nitrous oxide, and various halogenated compounds. Carbon dioxide is the most prominent greenhouse gas in Earth's atmosphere. Consequently, greater focus has been placed on managing CO₂ emissions.

Various carbon dioxide capture and storage technologies are being studied worldwide in order to mitigate global warming in the relatively short term. This concept includes separation and compression of CO₂ from industry and power plants, and transportation of CO₂ to a suitable storage site.

Many methods have been conceived for permanent storage of CO₂. These include gaseous storage in various deep geological formations (including saline formations and exhausted gas fields), liquid storage in the ocean, and solid storage by reaction of CO₂ with metal oxides to produce stable carbonates called as a mineral carbonation. Mineral carbon dioxide sequestration is a chemical storage route in which CO₂ is bound in a carbonate mineral. In nature, 100 million tonnes of carbon per year are bound by silicates. It is a natural weathering process, but very slow and may take thousands to millions of years.

The idea of carbon dioxide sequestration by minerals was originally proposed by Seifritz in 1990 [1] and first studied in detail by Lackner [2]. The suitable silicates mineral feedstock are olivine (Mg,Fe)₂SiO₄, forsterite Mg₂SiO₄, fayalite Fe₂SiO₄, enstatite MgSiO₃, diopside CaMgSi₂O₆, talc Mg₃Si₄O₁₀(OH)₂, serpentine Mg₃Si₂O₅(OH)₄, etc.

The theoretical gas-solid and gas-liquid carbonation reactions for these silicates can be described by the following equations:



Activation processes based on high-energy milling (mechanical activation) are used to modify the properties of materials, enhance the reactivity of materials and produce advanced materials as a result of changing their solid-state properties. High-energy milling is now one of the materials processing methods that are widely used in powder technology. The advantage of high-energy milling is its simplicity and effectiveness [3].

The aim of this paper is to compare properties of non-activated and mechanically activated olivine in a high-energy ball mill and describe the influence of mechanical activation of olivine on its carbonation.

Experimental

Material

Original olivine concentrate from Norwegian mining company North Cape Minerals (Åheim in Norway) was used as a raw material for the experiments.

Pure olivine contains approximately 93% forsterite (Mg₂SiO₄) and 7% fayalite (Fe₂SiO₄), corresponding to 51,7% MgO [4]. As the olivine concentrate is produced by crushing and sieving dunite, small amounts of accessory minerals like chlorite, chromite, enstatite, serpentine and talc can also be found in the final product. The olivine product used in this study is a foundry sand and contains approximately 95% pure olivine.

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Table 1. The chemical analysis of the original olivine concentrate

Constituent	Chemical analysis (wt. %)
MgO	50.2 %
SiO ₂	41.5 %
Fe ₂ O ₃	7.41 %
Al ₂ O ₃	0.36 %
NiO	0.33 %
Cr ₂ O ₃	0.30 %
MnO	0.08 %
CaO	0.08 %
Na ₂ O	0.01 %
K ₂ O	0.01 %
Loss on ignition	0.27 %

Mechanical Activation and Carbonation

Four series of experiments were conducted in which the original olivine concentrate was subjected to mechanical activation. The series was comprised of combined activation/carbonation experiments by dry and wet milling where the effect of activation and addition of water on the uptake of carbon dioxide was studied. Mechanical activation of the olivine concentrate was achieved using a Fritsch Pulverisette 6 planetary mill working in a dry mode (0% H₂O) and wet mode (50 % H₂O). 18 g of the feed material was activated in a 250 cm³ tungsten carbide mill chamber. The milling was conducted at 450 rpm using 50 tungsten carbide balls with 10 mm diameter and total weight of 360 g.

Experimental series, exposure of pure carbon dioxide to olivine were performed by pressuring the mill chamber containing the olivine and the milling balls with CO₂ gas immediately prior to milling. The duration of simultaneous milling and carbon dioxide exposure of the original olivine concentrate was 3 min. On completion of milling, the chamber was depressurized before the lid was opened and the final products were retrieved. Conditions of mechanical activation and carbonation are given in Table 2.

Specific Surface Area

The specific surface area was determined by the low temperature nitrogen adsorption method in a Gemini 2360 sorption apparatus (Micromeritics, USA).

Infrared Spectroscopy

The Infrared Spectroscopy (IR) spectroscopy measurements were carried out using a FT-IR Avatar 330 spectrometer (Thermo-Nicolet, USA) using KBr technique for preparation of samples.

Determination of Total Organic Carbon

The total carbon content of the materials produced from carbonation experiments were determined using a high temperature total organic carbon analyser Dohrmann-Rosemount DC-190 (USA) equipped with direct non-dispersive infrared gas analyzer.

Table 2. Experimental conditions and results of the activation and carbonation experiments

Sample	Milling time, min	Atmosphere	H ₂ O (%)	S _A (m ² .g ⁻¹)	C (%)
0	0	-	-	0.3	0
1	30	Air	0	5.2	0.19
2	30	CO ₂	0	4.0	0.39
3	5	Air	50	11.6	0.09
4	5	CO ₂	50	14.2	0.20
5	30	Air	50	41.8	0.25
6	30	CO ₂	50	39.9	0.67

Results and Discussion

Mechanical Activation

The results of mechanical activation of olivine concentrate are given in Table 2. The increase in specific surface area for the olivine sample after milling was noticed. Special effect was observed by milling in the presence of water. After 5 min milling in presence of H₂O specific surface area increase from value 0.3 m².g⁻¹ to 11.60 m².g⁻¹ (in air) and to 14.2 m².g⁻¹ (in CO₂). Value of specific surface area without water increases only to 5.2 m².g⁻¹ (in air) and to 4.0 m².g⁻¹ (in CO₂) after 30 min of milling. By addition of water the higher values for specific surface area have been obtained. The new surface formation is affected by the time of mechanical activation and the milling conditions such as addition of water.

Carbonation

The total carbon content of the materials produced from carbonation experiments is given in Table 2. There is a difference in CO₂ capture when air and CO₂ atmosphere has been applied during milling. The CO₂ capture is 2-3-times higher when CO₂ atmosphere was used. Moreover, the presence of H₂O has two effects: increase in surface area values as well as increase in CO₂ capture. The first effect is connected with traditional differences in dry and wet milling [5]. The second effect can be connected with change of CO₂ capture mechanism and has to be elucidated (Fig. 1 and 2).

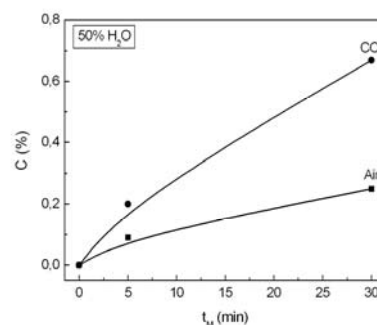


Figure 1. Total organic carbon C in olivine after milling by wet mode in air and CO₂ as a function of milling time t_M

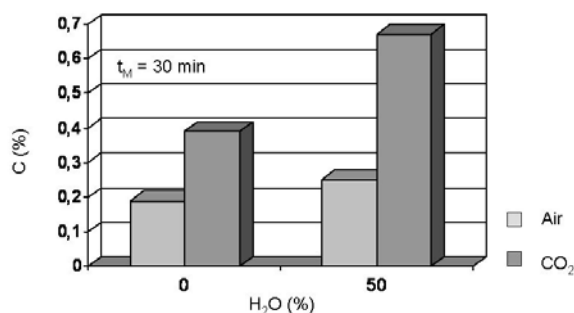


Figure 2. Total organic carbon C in olivine after 30 min milling by dry and wet mode in air and CO₂.

Figures 3 to 5 show the infrared spectra of non-activated (0) and mechanically activated olivine (Samples No.1-6 in Table 2) by dry and wet milling in two atmospheres, air and CO₂. We can identify some regions of the IR-bands. In the first region, there is an intensive band with a maximum at 3500 cm⁻¹ and it corresponds to OH⁻ vibrations due to hydration of olivine. No differences in intensity of this band have been detected for samples without or with application of the drying step during preparation of samples for IR measurements. Therefore, the water molecules seemed to be bound by chemisorption. The intensity of this band rises with increasing of olivine disordering by milling. The second region with 1100 – 500 cm⁻¹ is characteristic for olivine [6-8]. There is the same tendency in shape of spectra as described for the first region.

There are 3 bands in the third region. However, none of them is intrinsic to the non-activated olivine and their appearance is connected with the mechanical activation. The band at 1630-1650 cm⁻¹ belongs to H₂O vibration mode. Double peak in the range 1510–1420 cm⁻¹ (Fig. 3) overlaps the characteristic double peak in the 1515 – 1430 cm⁻¹ region which is attributable to carbonate absorption [9-13] as a consequence of the presence of CO₂ during milling.

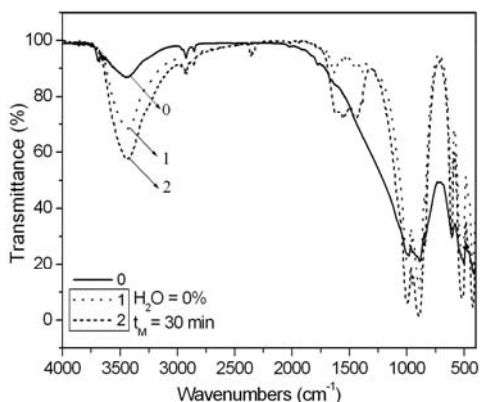


Figure 3. FT-IR spectra of olivine: as received (0), after 30 min of milling by addition 0% of H₂O in air (1) and in CO₂ atmosphere (2)

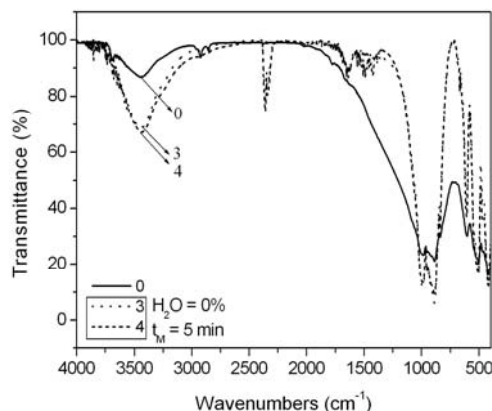


Figure 4. FT-IR spectra of olivine: as received (0), after 5 min of milling by addition 50% of H₂O in air (3) and in CO₂ atmosphere (4)

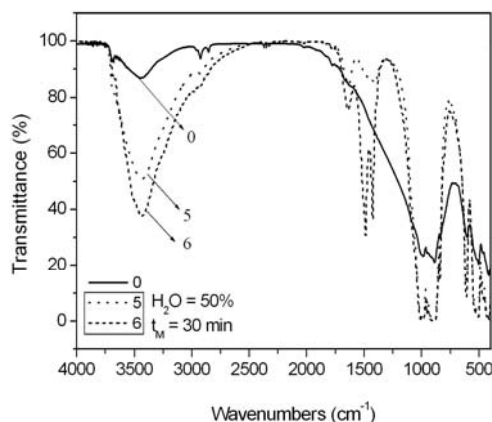


Figure 5. FT-IR spectra of olivine: as received (0), after 30 min of milling by addition 50% of H₂O in air (5) and in CO₂ atmosphere (6)

Conclusions

Changes in the surface area of olivine samples were detected as a consequence of milling. Milling in the wet mode shows the higher values of specific surface area. The infrared spectroscopy method offers a possibility to monitor carbonate absorption.

Acknowledgments

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