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Investigation of milling energy input on structural variations of processed olivine powders for CO_2 sequestration

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ABSTRACT

This study aims to identify the correlation between microstructure of mechanically processed olivine powders and the milling energy input, for an ultimate purpose of optimizing the ball milling approach for achieving the best CO_2 sequestration characteristics. Powders were processed in a high energy magneto ball mill. A variety of instrumental techniques such as scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) and X-ray diffraction (XRD) were utilized to characterize the particle size, specific surface area, pore volume, crystallinity and crystallite size of processes powders obtained with different levels of milling energy input. In each case, the variation of microstructural parameters with milling energy is compared for different milling devices extracted from the literature. Structural parameters of activated powders are correlated as a function of milling energy input, regardless of the ball mill type. The optimal range of milling energy input, expected to achieve the most desirable microstructure for CO_2 sequestration is found to be about 55 kJ/g.

1. Introduction

Fossil fuels are still the primary energy source in the world. The growing energy demand has led to an increasing fuel consumption which releases a huge amount of CO_2 into atmosphere as a result of combustion [1]. As reported by the International Energy Agency 13.1 gross tonnage of CO_2 was emitted from the combustion of coal between 2009 and 2010 [2]. Besides, CO_2 is also released by the natural activities such as the respiration of living species, plants, and microorganisms, decay of organic material, volcanic outgassing and forest fires [3]. CO_2 is known as the greenhouse gas with the greatest contribution to global warming. Therefore, CO_2 capture is an essential approach to control the global temperature variation [1–6]. Several methods have been suggested to reduce CO_2 emission while the mineral sequestration has drawn much attention because it is one of few approaches which converts carbon directly to its most thermodynamically stable state [4,7,8]. With this technique, minerals react with CO_2 and form a thermodynamically stable carbonates that prevent CO_2 emission in the atmosphere and the permanent CO_2 sequestration is achieved [3,4,6,9].

The ultramafic minerals are a promising candidate for mineral sequestration because they are very rich in magnesium oxides which are bound with other oxides in a silicate matrix [1]. Among these ultramafic minerals, olivine (magnesium silicate) is known to be one of the most ideal reactant for investigating CO_2 sequestration as it is an abundant natural mineral with a high reactivity [3,10]. Although the CO_2 mineralization process is thermodynamically favorable, the rate of reaction is usually very slow and it is not industrially feasible without pretreatment [3,6,11].

Direct carbonation of solid olivine can be performed in dry CO_2 gas. In a dry process direct gas/solid reaction occurs as described by Eq. (1) [4,12]

$$Mg_2SiO_4(s) + 2CO_2(g) \leftrightarrow 2MgCO_3(s) + SiO_2(s) \quad (1)$$

where s – solid and g – gas.

This reaction could be accelerated in the presence of water steam, as it activates the olivine surface by producing $Mg(OH)_2$ as an intermediate product (Eq. (2)), which reacts with CO_2 to produce $MgCO_3$ (Eq. (3)) [3]

$$MgO(s) + H_2O(g) \leftrightarrow Mg(OH)_2(s) \quad (2)$$

$$Mg(OH)_2(s) + CO_2(g) \leftrightarrow MgCO_3(s) + H_2O(g) \quad (3)$$

Alternatively, carbonation of olivine can also be carried out through wet (aqueous) processes. Wet carbonation includes dissolution of CO_2 in water and creation of carbonic acid (H_2CO_3) which reduces the pH of medium (Eq. (4)). Olivine is dissolved in an acidic medium and Mg^{+2} is liberated from the mineral matrix by H^+ (Eq.

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(5)). Subsequently, the Mg^{+2} ions react with bicarbonate (HCO_3^-) and precipitate as magnesite ($MgCO_3$) (Eq. (6)) [4,12]. The sequence of reactions is as follows:

$$4CO_2(g) + 4H_2O(l) \leftrightarrow 4H_2CO_3(aq) \leftrightarrow 4HCO_3^-(aq) + 4H^+(aq) \quad (4)$$

$$Mg_2SiO_4(s) + 4H^+(aq) \leftrightarrow 2Mg^{2+}(aq) + SiO_2(s) + 4H_2O(l) \quad (5)$$

$$2Mg^{2+}(aq) + 2HCO_3^-(aq) \leftrightarrow 2MgCO_3(s) + 2H^+(aq) \quad (6)$$

where aq – aqueous and l – liquid.

Dissolution of olivine (magnesium silicate) (Eq. (5)) is known to be an important step that determines the reaction rate and improves the total kinetics of carbonation process [4,12,13]. Structural parameters of minerals can also control the dissolution rate of minerals. As an example, the dissolution rate of forsterite could be affected by specific surface area (SSA) as well as its reactive surface sites [14]. Also, another research on the effect of crystallinity on the dissolution rate of SiO_2 shows that the rate limiting factor in dissolution of SiO_2 is breaking the Si–O bond and thus amorphization can improve the kinetics of dissolution of minerals (e.g. olivine) as it causes disordering which weakens the Si–O bond resulting in less resistance to dissolution [15].

In the literature several pretreatment methods have been developed to accelerate the rate of mineralization including the thermal activation, chemical activation, use of additives, combined high temperature – high pressure processes, and mechanical milling [12]. Mechanical milling (or ball milling) improves the kinetics of mineralization, by modifying the structure and reactivity of minerals [4–16]. It changes the microstructural parameters of minerals such as the particle size, specific surface area, crystallinity and crystallite size, resulting in a high level of structural disordering which facilitates CO_2 sequestration [9,11]. Thus, the investigation of the effect of milling parameters on the microstructure of minerals is necessary to optimize the activation process.

Several researchers have evaluated the influence of milling conditions on structural properties. Haug [12] investigated the effect of mechanical milling on olivine microstructural characteristics such as the particle size, specific surface area and crystallinity. It was reported that the effect of different milling processes on the carbonation properties of olivine samples was significant when a planetary mono mill, laboratory ball mill, Hicom 15 mill, and attritor mill were utilized. In particular, Haug [12] compared the conversion percentage after direct wet carbonation for 2 h of olivine samples that were initially ball milled in a Fritsch Pulverisette 6 mill. The conversion percentage was calculated by considering the molar ratio of precipitated carbonate ($(Mg, Fe)CO_3$) to available Mg and Fe (Fe, Mg) in olivine. They reported that the conversion percentage increased from 25% to 32% with the increase of milling time from 10 to 60 min. They suggested a correlation between the amount of amorphization and dissolution rate the latter given by Eq. (5).

In another study by Kleiv and Thornhill [16], the effect of structural changes on reactivity of mechanically milled olivine powders was evaluated. Mechanical milling was performed by a planetary mono mill and the effect of structural disordering on the increase of olivine powders reactivity was analyzed using XRD analysis [16]. Based on this study, relative to the samples that were milled for 1 min, the 60 min milling duration increased the dissolution rate by a factor of 9.0 [16]. The authors claimed that the observed dissolution rate was correlated to SSA.

The influence of ball milling was also investigated in a planetary mono mill running at 450 rpm and the reactivity of samples was compared after 6 h carbonation under ambient temperature and 60 bar pressure. In that study, the effect of mechanical milling on the increase of material's affinity for CO_2 sequestration was identified by Turianicová et al. [17]. They investigated both dry milled and unmilled samples after wet carbonation and reported no trace of carbonation on unmilled samples while the samples that were mechanically milled for 30 min before carbonation showed clearly visible carbonate peaks as evidence of CO_2 sequestration [17]. Unfortunately, Turianicová et al. [17] did not provide any specific correlation between the enhanced wet carbonation and microstructural parameters brought about by ball milling.

Other researchers also reported [18,19] that the wet/dry carbonation rate was increased by mechanical milling.

Although a number of investigations have been performed to study these structural variations occurring as a result of mechanical milling, a comprehensive study which correlates these variations with the milling energy input is still lacking.

In the present study the olivine powders are processed in a magneto ball mill and structural changes are studied as a function of milling energy input. The ball milled olivine powders were characterized using scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and the Brunauer–Emmett–Teller analysis (BET) methods to evaluate the particle size, specific surface area, pore volume, crystallinity (%) and crystallite size. The main purpose of this research is to identify a quantitative correlation between the milling energy input and structural variations. This is expected to be used as a comprehensive factor for most mechanical activation processes, regardless of the milling type, because for a known milling mode and ball to powder mass ratio, milling energy input per unit mass of powder is the single factor that includes all the other effective parameters such as mill geometry, milling time etc. For this purpose, structural changes in the milled samples are examined as a function of milling energy input. The derived trend of each property's variation is then used, by comparison with other reported milling types, to find the correlation between milling energy input and microstructural parameters of processed olivine samples. The outcome of this study can result in determining critical parameters as the process controlling factors for optimizing olivine structural activation and estimating the milling energy input range which could be applied for CO_2 sequestration experiments in the future.

2. Experimental

As received olivine powders were supplied by READE Advanced Materials, China. The bulk chemical composition of the olivine samples, before ball milling, was analyzed by means of energy-dispersive X-ray spectroscopy (EDX) using a Zeiss ULTRA Plus Scanning Electron Microscope equipped with a calibrated Pegasus 1200 energy-dispersive X-ray Spectroscopy (EDX) analyzer which revealed the olivine formula of $(Mg_{1.842}, Fe_{0.158})\ SiO_4$ with approximately 92 mol% forsterite (Mg_2SiO_4) and 8 mol% fayalite (Fe_2SiO_4).

Mechanical processing (ball milling) of olivine powders was implemented by controlled mechanical milling (CMM) in the magneto ball mill (Uni-Ball-Mill 5 manufactured by A.O.C. Scientific Engineering Pty Ltd., Australia) [20–22]. In this particular ball mill the milling modes with varying milling energy input can be achieved by using one or two strong NdFeB magnets, changing their angular positions and changing the number of hard steel balls in a milling vial.

Milling experiments were conducted in a stainless steel vial, operating under the impact mode at ~200 rpm. Four 25 mm steel balls of 65 g mass each were used for grinding. The total mass and the radius of the vial are 4030 g and 75 mm, respectively. Milling energy is adjusted by controlling milling time while the other milling parameters such as the ball to powder mass ratio, number of balls, milling mode, RPM and mass of powder are fixed. Details of milling energy variation as a function of milling time are explained in Section 3.1.

The SEM micrographs were obtained with the secondary electron detector using Zeiss ULTRA Plus Scanning Electron Microscope with the voltage of 10 kV. Samples were sputter coated with a thin layer of gold prior to SEM imaging to provide a conductive surface. Gold sputtering was performed via a UHV sputter system with the current of 20 mA and the duration of 139 s. SEM images were examined using an image processing and analysis program (Image J, Version 1.47 V, developed at the National Institutes of Health, USA) [23].

The X-ray diffraction (XRD) patterns were collected by a Bruker D8 diffractometer using a monochromated $CuK\alpha_1$ radiation ($\lambda = 0.15406$ nm) with the accelerating voltage of 40 kV and current of 30 mA. Diffraction data were recorded in the