Minerals Engineering 120 (2018) 66–74

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Effect of ball milling on the carbon sequestration efficiency of serpentinized peridotites

Ioannis Rigopoulos[a,*], Andreas Delimitis[b,1], Ioannis Ioannou[c], Angelos M. Efstathiou[d], Theodora Kyratsi[a]

[a] Department of Mechanical and Manufacturing Engineering, University of Cyprus, 1678 Nicosia, Cyprus
[b] Chemical Process & Energy Resources Institute (CPERI), Centre for Research & Technology Hellas (CERTH), 6th km Charilaou – Thermis Road, GR-57001 Thermi, Thessaloniki, Greece
[c] Department of Civil and Environmental Engineering, University of Cyprus, 1678 Nicosia, Cyprus
[d] Department of Chemistry, Heterogeneous Catalysis Lab, University of Cyprus, 1678 Nicosia, Cyprus

ARTICLE INFO

Keywords:
Ball milling
Carbon capture and storage (CCS)
CO_2 chemisorption
CO_2-TPD
Harzburgite
Mineral carbonation
Ultramafic rocks

ABSTRACT

Mineral carbonation has been suggested as a safe carbon capture and storage (CCS) strategy for the mitigation of climate change. This study investigates the effect of ball milling on the CO_2 sequestration capacity of peridotites, which are among the most promising readily available lithologies for CCS on the Earth's surface. A partially serpentinized harzburgite from the Troodos ophiolite (Cyprus) was subjected to different degrees of ball milling to produce nanoscale ultramafic powders with enhanced CO_2 uptake. The optimum ball milling conditions were found (16 h of wet ball milling with 50 wt% ethanol as process control agent) through CO_2 chemisorption followed by temperature-programmed desorption (CO_2-TPD) experiments. The results clearly showed that the CO_2 uptake of the initial rock material was increased by a factor of 4.5 after ball milling. Detailed characterization of the unmilled and ball-milled samples indicated that this enhancement is mainly attributed to (i) the reduction of particle size down to the nanoscale range and (ii) the structural disordering of the constituent Mg-silicate minerals due to mechanical deformation.

1. Introduction

The concentration of atmospheric CO_2 has been increased from a pre-industrial level of 280 ppm to 404 ppm in 2016 (NOAA-ESRL, 2017), primarily due to the widespread use of fossil fuels (Ciais et al., 2013; Keeling et al., 1995; Sawyer, 1972; Siegenthaler and Oeschger, 1987). This abrupt increase is considered to be the main reason for the observed global climate change (IPCC, 2005; Kuo et al., 1990), which seems to be largely irreversible on human timescales (Solomon et al., 2009). Thus, significant efforts have been made to develop efficient carbon capture and storage (CCS) technologies (e.g. Gislason and Oelkers, 2014; Lackner et al., 1995; Matter et al., 2016; Michael et al., 2010; Wilson et al., 2014). The recent COP21 Paris Agreement sets out a global action plan in order to put the world on track and avoid future dangerous climate changes by limiting the global warming to well below 2 °C above the pre-industrial levels (UNFCCC, 2016).

Mineral carbonation is a CCS technology that includes the conversion of CO_2 into carbonate minerals (Lackner et al., 1995; Oelkers et al., 2008; Olajire, 2013; Power et al., 2013; Sanna et al., 2014; Seifritz, 1990). It comprises the chemical reaction of rocks containing Mg and/or Ca-silicate minerals with CO_2 to form carbonate minerals, such as magnesite ($MgCO_3$), calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), which are stable over geologic time. Therefore, this carbon sequestration approach minimizes the risk of leakage and thus facilitates long-term and safe storage (e.g. Gislason and Oelkers, 2014; Matter and Kelemen, 2009; Matter et al., 2016; Seifritz, 1990). Peridotites are among the main sources of forsteritic olivine, which is the most promising mineral for carbon sequestration (O'Connor et al., 2005; Oelkers et al., 2008). The main carbonation reactions of peridotites are described by the following Eqs. (1)–(3):

$$\underset{\text{Forsterite}}{Mg_2SiO_4} + 2CO_2 \rightarrow \underset{\text{Magnesite}}{2MgCO_3} + \underset{\text{Silica}}{SiO_2} \quad (1)$$

$$\underset{\text{Enstatite}}{MgSiO_3} + CO_2 \rightarrow \underset{\text{Magnesite}}{MgCO_3} + \underset{\text{Silica}}{SiO_2} \quad (2)$$

* Corresponding author.
E-mail addresses: rigopoulos.ioannis@ucy.ac.cy (I. Rigopoulos), andreas.delimitis@uis.no (A. Delimitis), ioannis@ucy.ac.cy (I. Ioannou), efstath@ucy.ac.cy (A.M. Efstathiou), kyratsi@ucy.ac.cy (T. Kyratsi).
[1] Currently at the Department of Mechanical and Structural Engineering and Materials Science, University of Stavanger, 4036 Stavanger, Norway.

https://doi.org/10.1016/j.mineng.2018.02.011
Received 17 October 2017; Received in revised form 7 February 2018; Accepted 18 February 2018

$$\underset{\text{Serpentine}}{Mg_3Si_2O_5(OH)_4} + 3CO_2 \rightarrow \underset{\text{Magnesite}}{3MgCO_3} + \underset{\text{Silica}}{2SiO_2} + 2H_2O \quad (3)$$

The mineralization of CO_2 can be performed either *in situ*, by injecting CO_2 into ultramafic or mafic rocks (e.g. Matter and Kelemen, 2009; Matter et al., 2016), or *ex situ* in industrial reactors, after mining and crushing/grinding the rock material (e.g. Bodénan et al., 2014; Gerdemann et al., 2007; Rigopoulos et al., 2016a). *Ex situ* carbonation could provide a potential solution to sequester CO_2 from small to medium capacity emitters, where geological storage is not a viable option (Sanna et al., 2014). The major challenges of *ex situ* mineral carbonation are the scale of mining operations, the high energy consumption and the slow reaction kinetics (Gerdemann et al., 2007). Several studies have been performed to speed up the *ex situ* carbonation reactions by: (i) grinding/milling the rock materials, (ii) increasing the temperature, and (iii) dissolving the rock material in various solutions (e.g. Declercq et al., 2013; Haug et al., 2010; Li and Hitch, 2016a; Rigopoulos et al., 2015a, 2015b, 2016a, 2016b). In addition, many works have focused on the *ex situ* carbon mineralization of industrial wastes (e.g. mine tailings, construction waste), which could contribute to the reduction of atmospheric CO_2 concentrations and result in a number of economic benefits for many industries (Li and Hitch, 2017a; Power et al., 2013; Sanna et al., 2014; Wilson et al., 2014). An additional advantage of such a process is that it could reduce the hazardous nature of certain wastes, such as asbestos minerals (Bobicki et al., 2012). Emphasis should also be placed on the fact that the final products of mineral carbonation could be used by the construction industry as additives in order to render the whole approach more economically viable.

During the last decade, several studies focused on the application of milling techniques to olivine (Baláž et al., 2008; Haug et al., 2010; Kleiv and Thornhill, 2006, 2016; Li and Hitch, 2016a; Turianicová et al., 2013). However, only a few works have performed experiments using partially altered olivine-rich rocks (i.e. basalts, dunites) (Rigopoulos et al., 2015a, 2016a, 2017), which are much more abundant on the Earth's surface compared to pure olivine. In addition, the effect of mechanical activation on the carbon sequestration efficiency of ultramafic rocks/mine waste materials has been thoroughly studied by Li and Hitch (2016b, 2016c, 2017a, 2017b).

The aim of this paper is to assess the effect of the ball milling process on the CO_2 uptake of partially serpentinized harzburgites, which are among the most important rocks for the mineralization of CO_2 due to their relatively high content in forsterite-rich olivine. Although harzburgite is less reactive compared to dunite, it can be found in significantly larger quantities worldwide. In the framework of this study, we performed several ball milling experiments to produce ultrafine powders of high surface areas and determine the optimum ball milling conditions for harzburgites. The experiments were performed using a planetary ball mill, since this type of mill is commonly used for the production of ultrafine powders. The results obtained were then used to explain the effect of ball milling on the CO_2 chemisorption (uptake) over these nanoscale ultramafic materials.

2. Materials and methods

2.1. Sample selection, preparation and characterization

In the present study, a sample of harzburgite was collected from the western part of the Troodos mantle section (north of Mount Olympos; Fig. 1) for the preparation of nanoscale ultramafic materials with enhanced CO_2 uptake.

The Troodos ophiolite complex (Fig. 1) is the most intact ophiolite worldwide. It was formed in a supra-subduction zone environment around 92–90 Ma ago (Cenomanian-Turonian), based on U-Pb isotopic dating of plagiogranites (Mukasa and Ludden, 1987; Robertson, 2002; Robinson and Malpas, 1990). Its mantle section is divided into two units (Batanova and Sobolev, 2000). The eastern unit consists of spinel lherzolite with dunite bodies and zones of clinopyroxene-bearing harzburgite, while the western unit is principally composed of clinopyroxene-poor harzburgite and dunite. Above these mantle rocks, cumulate ultramafic and mafic lithotypes are found, which are cut by gabbroic intrusives; the upper massive gabbros locally include small plagiogranite bodies. Upwards, the sheeted dyke complex trends nearly N-S (Robertson, 2002). The overlying pillow lavas are traditionally divided into the "Lower" and "Upper" Pillow Lava units (LPL and UPL) (Gass and Smewing, 1973).

The mineralogical and textural characteristics of the studied rock sample were determined by petrographic analysis of a representative

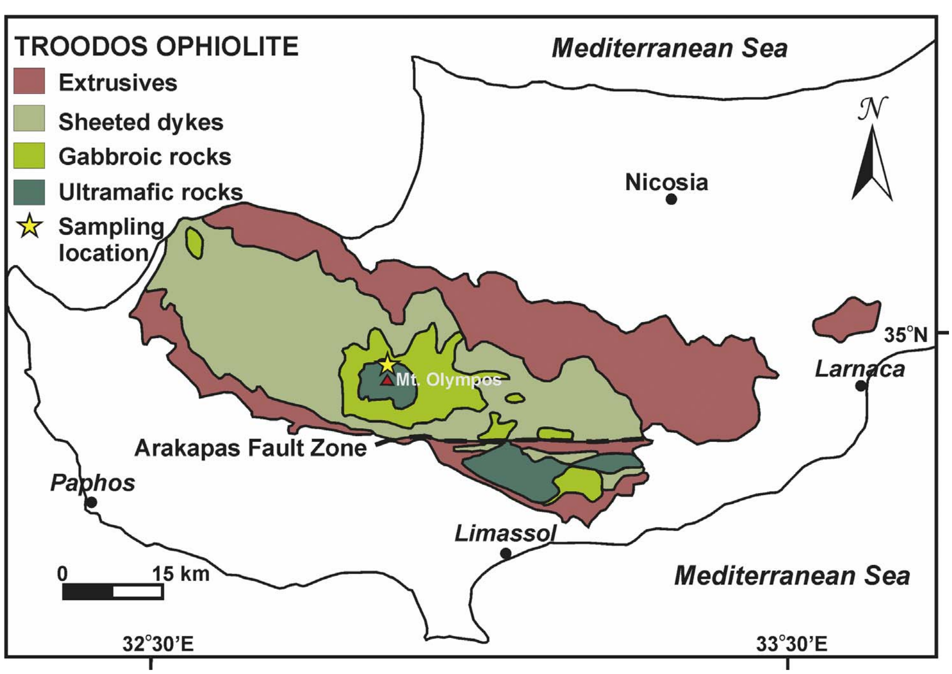

Fig. 1. Simplified geological-sampling map of the Troodos ophiolite, modified after Pearce and Robinson (2010).