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Short communication

Mechanical activation of ultramafic mine waste rock in dry condition for enhanced mineral carbonation

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ABSTRACT

This study examines mechanical activation as the pre-treatment method for ultramafic mine waste containing olivine and serpentine. Specific surface area, microstructure and carbonation conversion in a direct aqueous carbonation process were measured to test the effects of mechanical activation. It was found that, as a result of the grinding energy input on materials, surface area was increased, crystallite size was reduced and microstrain was accumulated, carbonation conversion was enhanced. With the presence of serpentine content, the formation of new surface area was promoted and the disordering of forsterite structure was prevented. Forsterite makes up the majority of the content and contributes to CO_2 sequestration under selected carbonation conditions. For the purposes of mineral carbonation, the mechanical activation of mine waste is preferable to simply grinding pure olivine.

1. Introduction

In order to mitigate the effects of climate change, a worldwide effort is being launched to use mineral carbonation with respect to the permanent storage of CO_2 for small and medium-sized industrial emitters (<2.5 Mt CO_2) (Sanna et al., 2014). However, mineral carbonation is currently not yet economically viable for large scale deployment. To reduce the cost of mineral carbonation, using ultramafic mine waste rocks or tailings as CO_2 feedstock arouse the interest among researchers recently (Hitch and Dipple, 2012). The waste rocks from ultramafic mine, such as nickel mine, usually contains olivine (Mg_2SiO_4) and/or serpentine ($Mg_3Si_2O_4(OH)_4$) (Hitch et al., 2010). And their carbonation process can be described in reactions (1) and (2), respectively.

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 \quad (1)$$

$$Mg_3Si_2O_4(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \quad (2)$$

To enhance the rate of mineral carbonation at any specific ultramafic mine site, it is important to develop individualized methods for their particular waste mineralogy. Research up to now, demonstrates that various carbonation routines have been developed, including direct or indirect carbonation route at gas-solid or aqueous phase (Sanna et al., 2014). The direct aqueous carbonation by O'Connor et al. (2005), is commonly considered as the state-of-art, which, although not economically competitive at this point in time, is used to compare technologies. The pre-treatment method that could activate both olivine and serpentine is mechanical activation at ambient temperatures and pressures.

Mechanical activation uses mechanical force to accelerate a downstream process, through induces changes in the surface properties and crystal structures of minerals. Until recently, research on mechanical activation has focused on comparing individual mineral responses to various grinding conditions (Rigopoulos et al., 2015; Sanna et al., 2013). However, the mechanical activation on mine waste with various mineralogy was rarely studied (Li and Hitch, 2015).

The aim of the present paper is to investigate the physical, structural and chemical properties of mine waste and which has been subjected to intensive dry milling. Different types of experimental techniques will be used to recognize mechanically-induced changes in mine waste.

2. Materials and experiments

The mine waste rock (TAW) was provided by Hard Creek Nickel Corp. from their Turnagain deposit in northern British Columbia, Canada. The olivine foundry sand (TSO) was obtained from the Twin Sisters Deposit in northwest Washington State, USA. TSO samples were used as a control. The starting materials for mechanical activation have a top size of 106 µm. X-ray powder diffraction

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Table 1
Variation of BET surface area (S_{BET}), crystallite size (D_V), microstrain (ε), and carbonation conversion (R_X) with mechanical activation time (t_{MA}) and specific milling energy (W_N).

Material	t_{MA} (min)	W_N[a] (kW h/t)	S_{BET} (m^2/g)	Forsterite		Lizardite		R_X[b] (%)
				D_V (nm)	ε ($\times 10^3$)	D_V (nm)	ε ($\times 10^3$)	
TSO	0	0	0.8	135.00	0.28	–	–	6.1
	30	900	2.4	83.32	0.46	–	–	17.9
	60	1800	2.6	85.34	0.45	–	–	24.9
	120	3600	2.7	74.35	0.51	–	–	22.5
TAW	0	0	3.1	91.4	0.42	28.4	1.34	8.7
	30	900	9.9	87.1	0.44	23.4	1.62	19.8
	60	1800	12.4	84.6	0.45	22.1	1.72	25.7
	120	3600	14.3	86.7	0.44	18.5	2.05	31.7

[a] W_N is the energy transferred to the powder, which is calculated according to Haug (2010).

[b] R_X is the percentage stoichiometric conversion of Mg^{2+}, Ca^{2+} and Fe^{2+} cations in silicate feed to carbonate, which is calculated according to Penner et al. (2004).

(XRPD) detected TAW contains 64.7% forsterite, and 29.6% lizardite, and TSO contains 97.9% forsterite.

The mechanical activation tests were conducted using a planetary ball mill (Micro Mill Pulverisette 7, Fitsch GmbH, Germany). In each test, 10 g of feed material was ground with seven 15 mm balls in a 45 mL mill bowl under a dry atmospheric condition. The rational speed of the mill was kept constant at 500 rpm.

The carbonation tests were conducted in a 100 mL Hastelloy-4566C Parr bench-top stirred autoclave (Parr Instruments, Moline, IL, USA). In each test, 7.5 g of samples were mixed with 50 mL solutions containing 1 mol/L NaCl and 0.64 mol/L $NaHCO_3$. The sample slurry was carbonated at 185 °C and 6 MPa CO_2, with a stirring speed of 1500 rpm for 1 h. The carbonation condition was chosen according to the optimum conditions for the direct aqueous mineral carbonation of olivine (O'Connor et al., 2005), except for the working pressure which was reduced from 15 MPa to 6 MPa due to the CO_2 supply was from a gas cylinder without the aid of a booster pump.

The specific surface area was measured using a nitrogen adsorption instrument (Autosorb-1MP, Quantachrome, Boynton Beach, USA) at 77°K and calculated using Brunauer–Emmett–Teller (BET) method. X-ray diffraction data were collected using a Bruker D8 Focus Bragg-Brentano diffractometer (Bruker AXS GmbH, Germany) working at a step size of 0.03° over the two theta range of 3–80° with CoKα radiation. X-ray powder diffraction data for the sample were refined using the Rietveld program Topas 4.2 (Bruker AXS GmbH, Germany). The procedures for quantitative analysis are the same as those found in Wilson et al.'s (2006) study. The microstructure characterization follows with respect to Li and Hitch (2016) using Eqs. (1) and (2):

$$D_V = \lambda / \beta_S \cos\theta \tag{3}$$

$$\varepsilon = \beta_D / \tan\theta \tag{4}$$

where D_V is the crystalline size, ε is the microstrain, λ is the wavelength, β_S is the total-size-integral breadth, and β_D is the total-strain-integral breadth.

3. Results and discussions

3.1. Mechanical activation effects

Mechanical activation of TSO and TAW was performed in the planetary mill, and the dependence of net specific milling energy W_N, BET surface area S_{BET}, crystallite size D_V, microstrain ε, and carbonation conversion R_X of the samples on the time of mechanical activation t_{MA} is listed in Table 1. The data shows that the S_{BET} of both materials increased with grinding time up to 60 min. Afterwards, the S_{BET} of TSO nearly unchanged, while that of TAW keeps increasing. The S_{BET} in mechanically-activated TAW is 4.2–5.2 times higher than in mechanically-activated TSO over the same period of t_{MA}. Table 1 shows a decrease in D_V, and an increase in ε of forsterite and lizardite in both TSO and TAW with the t_{MA} increasing. The D_V of forsterite in initial TAW is smaller than that in initial TSO. The extent of changes for forsterite in mechanically-activated TAW is not as distinct as it is for mechanically-activated TSO. It seems that the presence of serpentine content during mechanical activation, substantially enhance the formation of new surface, at the same time slightly prevents the disordering in microstructure of forsterite.

The R_X of both materials obtained from one hour of carbonation enhanced with the increasing of t_{MA}. The mechanical activation of TAW has a better R_X than does that of TSO with the same specific milling energy input. The changes in R_X of the two samples exhibited a similar trend up to 60 min of milling, afterwards the R_X of mechanically-activated TSO nearly unchanged and that of TAW keeps increasing, and reach 22.5% and 31.7%, respectively, after 120 min mechanical activation. The R_X for 120 min mechanically-activated TSO was comparable to that published in O'Connor et al. (2005) for olivine (−38 μm) under the same carbonation conditions. The R_X for 120 min mechanically-activated TAW was comparable to that published in O'Connor et al. (2005) for olivine (−38 μm) under high CO_2 partial pressure (15 MPa). It seems that the high reactivity of initial and mechanically-activated TAW is related to the presence of serpentine, which promotes the formation of new surface area. Similar beneficial effects were found in a study on in-situ CO_2 mineral sequestration in partially serpentine peridotites (Hövelmann et al., 2011).

3.2. Chemical changes

Fig. 1 shows the weight percentages of forsterite and lizardite in the initial and mechanically-activated samples. No new phases appeared in both materials during mechanical activation. After mechanical activation, the abundance of forsterite in TSO remains unchanged. However, the weight percentage of forsterite increased, while that of lizardite decreased in TAW with increased t_{MA}. Nearly 21.5% of the original lizardite content converted to forsterite after 120 min of milling. Similar finding was obtained in Zhang et al.'s study, that the molar ratio of dry mechanically-activated serpentine is equivalent to that of forsterite composition (Zhang et al., 1997).

Fig. 1 also shows the weight percentages of forsterite and lizardite in carbonated products of the initial and mechanically-activated samples. After carbonation, the ratio of lost weight in forsterite increased from 6.8% to 21.6% after 120 min of mechanical activation on TSO. The ratio of lost weight in forsterite increased from 6.4% in untreated TAW to 34.4% in 120 min mechanically-activated TAW. The ratio of lost weight in lizardite stayed constant at 14.39 ± 3.3% for up to 120 min of mechanical activation on TAW. It is possible that CO_2 sequestration using TAW resulted mainly from the carbonation of forsterite under laboratory conditions. This is congruent with the results of previous studies regarding the direct aqueous carbonation on mechanically-activated serpentine ore, as R_X did not show a distinct increase even after being attrited for an hour (Bobicki et al., 2015; O'Connor et al., 2005). As such, the enhanced R_X would be due to the mechanically-activated forsterite content in TAW. Thus, Mgs-silicate variety, forsterite, tends to be the major mineral in mine waste material, when choosing mechanical activation as the pre-treatment method for the direct aqueous carbonation process.