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Study of thermally conditioned and weak acid-treated serpentinites for mineralisation of carbon dioxide

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ABSTRACT

This contribution assesses the dissolution behaviour of serpentinite specimens, featuring distinct stages of serpentinisation, by treating the specimens with aqueous solutions of formic acid. We have observed a marked improvement in the extraction of magnesium when the samples were finely ground and thermally conditioned before treatment with formic acid. An extraction of 42% for −25 μm particles activated at 700 °C (29% residual OH) could be obtained from the forsterite–lizardite bearing specimen whereas 66% of magnesium was leached out of the fully serpentinised antigorite mineral, which was crushed to a particle size of −53 μm and baked at 720 °C (36% residual OH). Combined results derived from FTIR and XRD indicate that heat activation between 500 and 720 °C results in a reorganisation of lizardite and antigorite to amorphised material, forsterite and silica. Unreactive enstatite forms from the amorphised material and silica once the heating temperature exceeds 800 °C. Semi-quantitative XRD analysis yields an estimate of the crystalline and non-crystalline (forsterite) fractions of the activated material, permitting approximation of relative rates of dissolution of amorphous and forsterite phases. Although FTIR provides important information on forsterite and silica formation, it cannot detect the amorphous material. Forsterite and amorphous phases alike dissolve in the weak acid but the formation of skins of the amorphous silica limits the overall magnesium yield on a laboratory time scale. The material that constitutes the skins originates from two sources: (i) silica formed in forsterisation of serpentine minerals undergoing heat treatment, and (ii) silica produced during extraction of Mg by a weak acid from amorphous and forsterite phases. Heat activation also leads to the formation of andradite and modified chlorite minerals that exhibit less solubility than forsterite and amorphous phases in weakly acidic medium.

1. Introduction

Mineral carbonation bears an analogy to the rock weathering process in nature, which involves the fixation of carbon dioxide, by formation of calcium and magnesium carbonates from mafic and ultramafic silicates. Thermodynamically and environmentally, stable solid carbonates could provide storage capacity for anthropogenic emissions of carbon dioxide over a geological time scale. Abundant suitable feedstocks such as magnesium-rich olivine and serpentine as well as wollastonite with high calcium content, are available worldwide. In addition pyroxenes, amphiboles, mine tailings and industrial residues represent potential sources of magnesium and calcium for carbonation purposes (Kodama et al., 2008; Teir et al., 2007). Australia harbours extensive deposits of serpentinite, largely composed of serpentine occurring in ultramafic rocks. The Great Serpentinite Belt and the Gordonbrook Serpentinite belt, both located in the New England Orogen as well as the Coolac Serpentinite Belt in the Lachlan Orogen, offer significant resources for carbon dioxide mineralisation in the state of New South Wales (Oskierski et al., 2013a, b), where serpentinite is primarily used as a flux in steel making.

In spite of its thermodynamic favourability, carbonation of olivine and serpentinite is plagued with extremely slow kinetics that hinder large scale implementation of the process, and necessitates activation of these rocks either by grinding or heat treatment. Several researchers attempted to decrease particle size through pulverisation, raise reaction temperature and pressure, change solution chemistry and use catalysts/additives to accelerate the reaction rate (Golubev et al., 2005; Krevor and Lackner, 2009; Golubev and Pokrovsky, 2006; Haug et al., 2011). In addition, serpentine minerals ($Mg_3Si_2O_5(OH)_4$) are activated by heating to

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between 600 and 750 °C that removes part of hydroxyl groups and amorphises the mineral structure, significantly increasing their reactivity to CO_2 (Balucan et al., 2013; Balucan, 2013; Balucan and Dlugogorski, 2013; see also a recent review by Dlugogorski and Balucan (2014)).

The most comprehensive studies so far outline two thermodynamically feasible aqueous mineral carbonation approaches. The first process, developed by the Albany Research Center, involves direct carbonation in aqueous solutions of 0.64 M $NaHCO_3$ and 1 M NaCl conducted at 150 bar CO_2 and 155 °C and 185 °C, for heat pre-treated serpentine and olivine, respectively (O'Connor et al., 2000, 2001). The second approach is based on two principal steps namely silicate dissolution, usually by acids, and carbonate precipitation (Oelkers and Schott, 2005). Since the former mechanism is generally assumed to be rate-limiting with respect to the overall carbonation process, many studies have focused on the extraction of calcium or magnesium from native minerals (Park and Fan, 2004; Carroll and Knauss, 2005; Hänchen et al., 2006).

Lackner et al. (1995) and subsequently Wendt et al. (1998), Park et al. (2003), Alexander et al. (2007) and Teir et al. (2009) demonstrated that strong acids (HCl, H_2SO_4, HNO_3 and H_3PO_4) could effectively leach out magnesium ions. However, this scenario is very energy intensive owing to the need for complex acid recycling processes. Another approach involves deploying a weak acid, such as acetic acid, as an accelerating medium for the artificial weathering of wollastonite with acid recycling occurring in a fashion that has been proposed to require less energy (Kakizawa et al., 2001). Other weak acids have been subject to less detailed studies. Teir et al. (2007) reported a Mg extraction of 88% and 93%, from a serpentine containing 40% MgO and an equal amount of SiO_2, using 4 M HCl and HNO_3, respectively, at 70 °C within 2 h; Krevor and Lackner (2009) achieved 60%, 80% and 100% Mg yield in 0.1 M sodium citrate, EDTA and sodium oxalate, respectively, at 20 bar of CO_2 and 120 °C from antigorite; Bałdyga et al. (2010) obtained a Ca extraction of 30% from wollastonite in acetic acid at 50 bar and 80 °C and 85% in succinic acid under the same conditions.

In the present study, we have sought to evaluate the propensity of serpentinites to liberate magnesium ions when subjected to a weakly acidic medium, in the absence of complexing agents. In a preliminary investigation (Ghoorah et al., 2010), we found formic acid as the most effective leaching medium (Ghoorah et al., 2010). Our experimental work was also geared towards the identification of optimal mechanical activation and thermal conditioning to ameliorate dissolution of samples of partially and fully serpentinised ultramafic rocks. XRD, FTIR, TGA-MS and ICP-OES, were employed to pin down the mineralogical, morphological as well as chemical changes occurring within the samples during activation and acid dissolution. However, investigating the technological steps and the costs involved in recycling the weak acid lie outside the scope of the present contribution, requiring a separate study. To the best of our knowledge there are no studies that have compared the behaviour of serpentinites, at different stages of serpentinisation, in a weakly acidic medium as we have done with a fully serpentinised and a partially serpentinised sample. Investigating the suitability of formic acid for Mg extraction from serpentinites adds another innovative aspect to the paper.

2. Material and methods

2.1. Analytical methods and description of starting material

For this study, we sampled serpentine specimens from Somerset mine in the Coolac Serpentine Belt and Abras mine, located, respectively, in south-eastern and north-eastern New South Wales, Australia. To investigate the effect of particle size reduction on the extent of dissolution, we crushed the coarse samples in a Fritsch pulverisette laboratory ball mill and sieved them into +75 μm, −75 μm, −53 μm and −25 μm fractions using an automatic sieve shaker for at least 15 min. Laser particle sizing of the ground and homogenised samples were performed in aqueous media on a Malvern Mastersizer Hydro 2000 SM (Fig. 1a and b). The apparatus was verified prior to measurements using standard glass beads with $D[v, 0.1] = 53.7 \pm 4$ μm, $D[v, 0.5] = 68.2 \pm 3$ μm and $D[v, 0.9] = 87.5 \pm 7$ μm. A symmetric distribution with $D[v, 0.1] = 52$ μm, $D[v, 0.5] = 69$ μm and $D[v, 0.9] = 91$ μm confirmed the accuracy of the results.

We afforded X-ray diffraction (XRD) measurements on a Philips X'Pert Pro diffractometer with Cu Kα radiation operated at a voltage of 40 kV and a current of 40 mA. A goniometer continuously scanned the samples from 6° to 90° 2θ with a step size of 0.008°. With respect to petrography, hand specimens were cut, impregnated with epoxy resin (araldite), polished and examined through a Zeiss Axioplan Universal Microscope equipped with a digital camera.

In addition, Fourier transform infrared spectroscopy confirmed the functional groups present in the fresh and treated samples. About 5 mg of ground material was dispersed in one or two drops of mineral oil (Nujol), purchased from Sigma Aldrich (Australia), to form a paste or mull, which was spread on a mid-infrared transparent KBr window and then placed in the spectrometer. We collected absorbance FTIR spectra with a Perkin–Elmer 100 spectrometer over the mid-infrared range from 400 to 4000 cm^{-1} wavenumber range at a resolution of 1 cm^{-1}. In all, 8 scans were summed for each spectrum. Nujol displays infrared absorption bands at 2920, 2853, 1457, 1378 and 722 cm^{-1}.

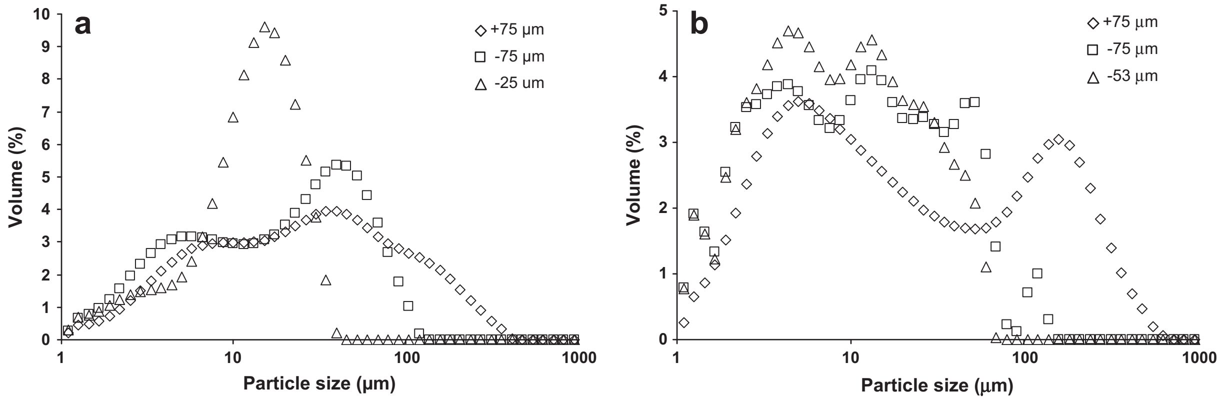

Fig. 1. Particle size distribution of (a) Somerset and (b) Abras serpentine samples that were used for experiments.