



Mineral carbon storage in pre-treated ultramafic ores



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ABSTRACT

Mineral carbon sequestration (MCS) is a type of carbon storage based on natural rock weathering processes where CO₂, dissolved in rainwater, reacts with alkaline minerals to form solid carbonates. Although MCS has advantages over other carbon storage techniques, an economic MCS process has not yet been developed. Two approaches were taken in this work to attempt to reduce the cost of MCS. The first approach was to use a waste material, serpentine waste from ultramafic nickel ore processing, as a feedstock. The second approach was to develop pre-treatments to increase the carbon storage capacity of the feedstock. Two pre-treatments were investigated in this work, including microwave pre-treatment and leaching with ligands at neutral to alkaline pH. The carbon uptake of ultramafic ores was found to increase with increasing microwave pre-treatment after a threshold heating time of 4 min was surpassed. A maximum carbon uptake of 18.3 g CO₂/100 g ore (corresponding to a carbonate conversion of 36.6%) was observed for microwave pre-treated ore. The increase in carbon uptake was attributed primarily to the conversion of serpentine to olivine in ultramafic ores that occurs as result of microwave pre-treatment. The effect of five different ligands (catechol, citrate, EDTA, oxalate and tiron) on the carbon uptake of ultramafic ores was investigated. Of the ligands tested, only catechol and tiron were found to both improve the leaching of magnesium from the ores and the quantity of CO₂ stored. A maximum carbon uptake of 9.7 g/100 g ore (corresponding to a carbonate conversion of 19.3%) was observed for ultramafic ore pre-leached and carbonated in tiron solution at pH 10. This is the first time ligands have been reported to improve the carbon uptake of mineral carbon sequestration feedstock. Although process optimization work was not conducted, both microwave pre-treatment and leaching with ligands at neutral to alkaline pH show promise as ways to lower the cost of MCS.

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1. Introduction

Carbon capture and storage (CCS) is a strategy that has been identified to reduce carbon dioxide (CO₂) emissions and mitigate climate change. Mineral carbon sequestration (MCS) is the only known form of permanent CO₂ storage (Lackner et al., 1995). MCS also has the potential to capture and store CO₂ in a single step, it can be used where geologic carbon storage is not feasible (Zevenhoven and Fagerlund, 2010), the products are environmentally benign, and valuable by-products, including magnesium carbonate and silica, can be produced during the process (Maroto-Valer et al., 2005). MCS is modeled on rock weathering processes where CO₂, dissolved in rain water, reacts with alkaline minerals to form solid carbonates. Although the reactions are thermodynamically favorable, in nature they occur over millennia (Huijgen

and Comans, 2003). The challenge of MCS is to accelerate the carbonation of mineral feedstock with minimal energy and material losses.

MCS may be achieved by reacting alkaline minerals with CO₂ directly in either the gaseous or aqueous phase, or indirectly by first extracting Mg²⁺ (or Ca²⁺) from minerals, separating the leached ions from the remaining solid phase, and then precipitating the ions as carbonates. Thus far, an economic MCS process has not been developed as all known MCS process schemes are energy intensive. Energy is used to prepare the feedstock, to drive carbonation at an acceptable rate, and to process the reaction products (Metz et al., 2005). In general, aqueous MCS schemes have been the most successful. The direct aqueous processes have involved fine grinding of the mineral feedstock, and in the case of serpentine, heat treatment (for dehydroxylation) to render the mineral sufficiently reactive (Gerdemann et al., 2007; O'Connor et al., 2005). The combination of grinding and heat treatment by conventional means has resulted MCS processes with net-positive CO₂ emissions (Gerdemann et al., 2007; Dlugogorski and Balucan,

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2014). Even after pre-treatment, the direct aqueous processes have required severe processing conditions to achieve high carbonate conversions (i.e. 15 MPa, 155–185 °C) (Gerdemann et al., 2007; O'Connor et al., 2000). The indirect aqueous processes, while achieving high carbonate conversions under mild processing conditions even when using serpentine as feedstock, are associated with exorbitant chemical costs (Krevor and Lackner, 2011; Teir et al., 2009).

Ways to reduce the cost of MCS include indentifying inexpensive and readily available mineral feedstocks, reducing the energy associated with grinding and activating mineral feedstocks, and reducing the chemical reagent requirements. The cost of MCS may be further offset by producing saleable carbonation by-products, such as precipitated magnesium carbonate and silica, and by storing CO₂ directly from flue gas streams, thereby skipping the capture step which has been estimated to cost between \$60 and \$100 per tonne of CO₂ avoided (Ho et al., 2011). The approach taken in this work to attempt to reduce the cost of MCS has been to select a waste product (serpentine waste from ultramafic nickel processing operations) as feedstock, and to develop pre-treatments that increase the CO₂ reactivity of the waste material. Two different pre-treatments were investigated including microwave pre-treatment and leaching with ligands.

1.1. Microwave pre-treatment

Microwave pre-treatment has been tested as a way to enhance both mineral processing and MCS operations. Microwave pre-treatment has been shown to successfully convert serpentine in the ores to olivine (Bobicki et al., 2014a), improve the grindability of some ores (Bobicki et al., 2013), and improve the rheology of ultramafic ore slurries (Bobicki et al., 2014b). It is believed the combination of improved grindability and rheology should improve the mineral processing of ultramafic ores. The effect of microwave pre-treatment on the carbonation of ultramafic nickel ores will be investigated in this work.

Microwave pre-treatment has been tested in a limited way by previous researchers for the enhancement of MCS. White et al. (2004) investigated the reactivity of CO₂ with serpentine at 1 bar and 375–650 °C in a gas–solid reaction in a microwave furnace, and the reaction of serpentine with bicarbonates in a microwave hydrothermal apparatus at 15 bar and 200 °C. Unfortunately, little reactivity was observed in these experiments. However, it is known both gas–solid and direct aqueous carbonation processes yield poor results at low pressures (Bobicki et al., 2012; Gerdemann et al., 2007). In this work, ultramafic ores will be pre-treated with microwaves, followed by direct aqueous carbonation at pressure and temperature conditions reported to be optimal for the carbonation of conventionally heat-treated serpentine (O'Connor et al., 2005; Gerdemann et al., 2007).

1.2. Leaching with ligands

The second pre-treatment, leaching with ligands, was tested as a way to promote the dissolution of serpentine in the ores/tailings for the enhancement of MCS without the need for a secondary pH adjustment. Five different ligands, including catechol, citrate, EDTA, oxalate and tiron, were tested for their capacity to improve the leaching of magnesium from serpentine in ultramafic ores at neutral to alkaline pH. The ligands tested were all found to improve the leaching of ultramafic ores in some capacity, with catechol, EDTA and tiron showing the most potential for enhancing MCS (Bobicki et al., 2014c).

While the dissolution of silicate minerals by ligands for the purpose of mineral carbon sequestration has been studied by a number of researchers (Krevor and Lackner, 2011; Bonfils et al.,

2012; Hänchen et al., 2006; Park et al., 2003; Prigobbe and Mazzotti, 2011; Declercq et al., 2013), few studies on the carbonation of ligand-leached minerals have been conducted, and none report the successful conversion of substantial Mg to carbonates. However, in studies where the carbonation of the ligand-leached material has been attempted (Krevor and Lackner, 2011; Bonfils et al., 2012), carbonation has been conducted at relatively low temperature (90–120 °C), low pH (acidic), and low CO₂ pressures (2 MPa). The approach in this work will be to carbonate ligand-leached slurries at temperature and pressure conditions reported to be optimal in direct aqueous processing schemes (O'Connor et al., 2005; Gerdemann et al., 2007), at neutral to alkaline pH where the precipitation of MgCO₃ will be favored.

2. Materials and methods

2.1. Mineral feedstock

Two ultramafic nickel ores were used as feedstock in this study. The “OK ore” was sourced from the Okanogan nickel deposit in Washington State, USA. The “Pipe ore” was obtained from the Thompson Nickel Belt in Manitoba, Canada. The elemental composition of the ores is given in Table 1. The ores were crushed to <2.5 mm using a jaw crusher (BB 200, Retsch, Burlington, ON, Canada) and milled to <1.0 mm with a disc mill (DM 200, Retsch, Burlington, ON, Canada). The <1.0 mm material was sieved using standard techniques to isolate the <45 µm and 0.425–1 mm size fractions. The 0.425–1 mm size fraction of both the OK and Pipe ores was split into 100 g samples for microwave pre-treatment and grinding using a Jones riffle sample splitter. The <45 µm material was split into 1 g samples using a spatula technique for the leaching work. While tailings are the target material for MCS feedstock, whole ores were used in this study because neither ore is currently being exploited for nickel production and tailings are not being produced, and due to the low grade, the tailings produced by the processing of the ores will be similar in composition to the whole ores.

2.2. Materials characterization

X-ray fluorescence (XRF) spectroscopy (Orbis PC Micro-EDXRF Elemental Analyzer, EDAX, Mahwah, NJ, USA) and inductively coupled plasma mass spectroscopy (ICP-MS) (Perkin Elmer Elan 6000, Waltham, Massachusetts, USA) were used to determine the elemental composition of the ores. ICP-MS was also used to determine the magnesium content of supernatant. Qualitative X-ray diffraction (XRD) (RU-200B Line Focus X-ray System, Rigaku Rotating Anode XRD System, Rigaku, ON, Canada) was performed to determine the mineral phases present in the ores before and after microwave pre-treatment, and before and after leaching with ligands. Quantitative XRD analysis was also performed on some samples by PMET Inc. of New Brighton, PA using the Rietveld refinement technique. Total carbon for the microwave-related tests was measured using a coulometric technique (UIC Coulometrics Total Carbon Analyzer, Joliet, IL, USA). Total inorganic carbon for the leaching-related tests was determined by subtracting the total organic carbon (acidification technique used) from the total

Table 1
Elemental composition of OK and Pipe ores.

Method	MgO XRF	CaO XRF	SiO ₂ XRF	Al ₂ O ₃ XRF	Fe ICP	Ni ICP	S CHNS
OK ore (wt.%)	45.8	0.8	40.7	1.1	4.6	0.26	0.66
Pipe ore (wt.%)	39.5	1.1	34.8	1.8	6.0	0.23	2.18

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