Strategies for enhancing carbon sequestration in Mg-rich mine tailings

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Abstract Mineralization of CO_2 within Mg-carbonate minerals in Mg-rich mine tailings provides the potential to render large mines greenhouse gas neutral. A potential strategy to enhance carbon fixation rates is through injection of CO_2-rich gas into tailings. Carbonation rates and CO_2 storage capacity must be sufficient to minimize CO_2 leakage to the atmosphere. Experimental carbonation rates of one tailings mineral, brucite, suggest that its carbonation can keep pace with mine emissions and that total carbon fixation rates are limited by tailings production. Because power consumption scales with tailings production, brucite contents of ≈ 6.5 % are needed to offset point source mine emissions.

Keywords CO_2 sequestration, mine tailings, carbonate precipitation, tailings management strategies, carbon mineralization

Introduction

Anthropogenic greenhouse gas (GHG) emissions, particularly CO_2 emissions, have been identified as a cause of global climate change (IPCC 2007). Carbon sequestration is one of many potential strategies to stabilize CO_2 concentrations and prevent irreversible climate change while we transition to non-fossil fuel based energy sources (Broecker 2007; Pacala and Socolow 2004). Mineral carbonation, or carbon mineralization, is a method of carbon sequestration that involves dissolution of non-carbonate minerals (*e.g.* silicates, hydroxides, and oxides) to release cations, and the binding of these cations with CO_2 in carbonate minerals (Lackner 2003; Lackner *et al.* 1997, 1995; Seifritz 1990). Many industrial wastes, including mine tailings, are rich in minerals that provide suitable feedstock for mineral carbonation such as brucite [$Mg(OH)_2$], forsterite [Mg_2SiO_4], and serpentine group minerals [$Mg_3Si_2O_5(OH)_4$] (*e.g.* Bobicki *et al.* 2012; Renforth *et al.* 2011; Wilson *et al.* 2009). Carbonation of industrial wastes is advantageous as it exploits available waste materials that are typically fairly reactive under ambient conditions, and it may decrease the hazardous nature of wastes such as asbestos mine tailings (*e.g.* Bobicki *et al.* 2012; Renforth *et al.* 2011). Carbon mineralization in mine wastes has been documented to occur passively under normal mining practices at both historic and active asbestos, diamond, chromite, and nickel mines globally (Bea *et al.* 2012; Beinlich and Austrheim 2012; Pronost *et al.* 2012; Wilson *et al.* 2011, 2010, 2009, 2006). Carbonation reactions are facilitated by high surface areas (Wilson *et al.* 2009), yet are limited by the uptake of CO_2 into solution (Wilson *et al.* 2010). Although the carbon sequestration capacity of ultramafic tailings is significant, rates of passive carbonation are insufficient to take full advantage of the carbon sequestration potential. For instance, complete carbonation of tailings produced annually at the Mount Keith Nickel mine (MKM) in Australia (≈ 11 Mt tailings per year; BHP Billiton 2005) would exceed annual mine emissions by more than a factor of ten. Yet passive carbonation rates currently offset annual emissions by only ≈ 15 % (Wilson 2009). Carbon mineralization in mine tailings could be accelerated by increasing the exposure of tailings to CO_2, such as by injection of CO_2-rich gas streams into tailings storage facilities. Here, we generalize the experimental results from our previous work (Harrison *et al.* 2013) investigating the potential for accelerated carbonation of brucite, a common and highly reactive tailings mineral, to evaluate CO_2 injection as a carbon sequestration strategy in mine tailings. Brucite is a Mg-hydroxide mineral that is typically present between 1 and 15 wt. % in ultramafic mine tailings and residues (Bea *et al.* 2012; Chrysochoou *et al.* 2009; Pronost *et al.* 2011). It is far more reactive than the more abundant silicate phases such as serpentine (*e.g.* Assima *et al.* 2013; Bales and Morgan 1985), and therefore provides a useful starting point for investigation of accelerated tailings carbonation strategies.

Methods

The effects of supplying CO_2-rich gas streams at ambient temperature and pressure (≈ 21 °C; 1 atm) on the carbonation rate of brucite was investigated experimentally in batch reactors, with geochemical conditions emulating those at MKM. Alkaline 3.0 L slurries containing 150 g brucite were supplied with gas streams with a range of CO_2 content (≈ 0.04 %, 10 %, 50 %, 100 % CO_2 by volume) at a rate of ≈ 270 mL/min (Harrison *et al.* 2013). Slurry samples were extracted periodically for measurement of pH, the stable carbon isotopic composition ($\delta^{13}C$) of dissolved inorganic carbon (DIC), and cation and DIC concentrations. Solid samples were collected for measurement of mineralogical compositions and $\delta^{13}C$. For further details regarding the experimental setup, refer to Harrison *et al.* (2013).

Results and Discussion

The experimental results indicated that brucite (brc) was carbonated to produce the hydrated Mg-carbonate mineral nesquehonite [$MgCO_3 \cdot 3H_2O$] at a rate that increased linearly with CO_2 partial pressure (pCO_2) according to the following reaction (Harrison *et al.* 2013):

$$Mg(OH)_{2(s)} + HCO_3^-{}_{(aq)} + H^+{}_{(aq)} + H_2O_{(l)} \longleftrightarrow MgCO_3 \cdot 3H_2O_{(s)} \qquad \text{(Eq. 1)}$$

A 2400-fold increase in CO_2 sequestration rate was achieved with an increase from atmospheric composition (≈ 0.04 % CO_2) to pure CO_2. Increasing the pCO_2 serves to enhance both brucite dissolution and carbonate precipitation. However, even at elevated pCO_2 the rate of CO_2 uptake into solution was found to be rate limiting. This is attributed to the relatively slow transformation from gaseous CO_2 to an aqueous form that can be mineralized (*i.e.* HCO_3^- and CO_3^{2-}) as indicated by chemical and isotopic disequilibrium between gaseous CO_2 and DIC during the carbonation reaction (Harrison *et al.* 2013). Nevertheless, the experimental carbonation rates would be sufficient to carbonate all the brucite produced annually at MKM (0.1-0.3 Mt brucite), offsetting total mine emissions by 20–60 % (Harrison *et al.* 2013). Therefore, accelerated carbonation of tailings minerals by supplying CO_2-rich gas streams is a promising method for reducing GHG emissions at mine sites with tailings that contain brucite. Power generation at mine sites often occurs at on-site power plants, which could provide a local point source of CO_2 emissions. Flue gas from power plants typically contains between 10–20 % CO_2 (Kikkinides *et al.* 1993; Uibu *et al.* 2011). These emissions provide a readily available source of CO_2-rich gas that could be injected into tailings storage facilities to accelerate brucite carbonation (Harrison *et al.* 2013). An alternative would be to circulate CO_2-rich water, which could help to avoid the issue of slow CO_2 uptake into solution. However, the use of CO_2-rich gas has the advantage that it would not increase the water consumption at mine sites, which can be an important concern particularly for mines in arid locations with high evaporative losses. A potential concern regarding CO_2 injection is its effect on the mobility of hazardous metals. Metals could be mobilized via dissolution of primary tailings minerals, yet secondary precipitates can incorporate these metals and limit their mobility depending on solution pH (Power *et al.* 2010). Therefore, further investigation is warranted to determine the potential side effects of CO_2 injection on tailings geochemistry.

If brucite carbonation via CO_2-rich gas injection were implemented at a mine site, tailings storage facilities would need to be designed to minimize leakage of injected CO_2 to the atmosphere. This requires that the rate of carbon mineralization in the tailings keep pace with the rate of CO_2 supply. The rate of CO_2 injection will be limited by the availability of the highly reactive phases such as brucite, as these will consume the majority of the CO_2 in the short term. Greater brucite content will accommodate higher injection rates, as well as provide greater total sequestration capacity. The sequestration or 'reactive capacity' (Eq. 2) of brucite is calculated by assuming complete conversion to nesquehonite; this equates to 0.75 g CO_2 stored per gram brucite. In order to prevent CO_2 leakage, the rate of CO_2 supply must not exceed the reactive capacity at any given time, and should therefore balance the rate of brucite deposition according to the reaction stoichiometry.

The rates achieved in the brucite carbonation experiments employing 10 % CO_2 were considered representative of reaction in mine tailings. The predicted brucite carbonation rate using flue gas is thus ≈ 0.3 mol CO_2/m^2 brc/a (after Harrison *et al.* 2013). Due to the relatively high reactivity of brucite, it is assumed that the rate of CO_2 mineralization is dictated primarily by the brucite carbonation rate rather than carbonation of the less reactive silicates. The reactive capacity provided by brucite and the time before CO_2 venting at a given CO_2 injection rate can then be calculated according to Equations 2 and 3. Carbonation rates in the field will be affected by water content distribution (*e.g.* Assima *et al.* 2013), surface passivation effects (*e.g.* Jeen *et al.* 2006), and the hydraulic properties of the porous medium. Quantification of the extent to which these effects will alter carbonation rates requires further experimentation. As such, for the purposes of this study, it is assumed that CO_2 supply is the primary rate-limiting factor; therefore Equation 3 applies only when the maximum rate of carbonation (Eq. 4) is less than the rate of CO_2 supply.

$$Reactive\ capacity\ (C_r) = \frac{m_t F_{brc}}{GFW_{brc}} b \qquad \text{(Eq. 2)}$$

$$Time\ to\ CO_2\ venting = \frac{C_r}{r_{CO_2}} \qquad \text{(Eq. 3)}$$

$$Maximum\ brucite\ carbonation\ rate = m_t F_{brc} S_{brc} r_{brc} \qquad \text{(Eq. 4)}$$

Where, C_r is the reactive capacity (mol CO_2), m_t is the mass of tailings (g), F_{brc} is the brucite content of the tailings as a fraction of tailings mass, b is a stoichiometric coefficient for the carbonation of brucite, GFW_{brc} is the molar mass of brucite (g/mol), r_{CO_2} is the rate of CO_2 supply (mol CO_2/a), S_{brc} is the surface area of brucite (m^2/g), and r_{brc} is the 'flue gas' rate of brucite carbonation measured in batch reactors (mol CO_2/m^2 brc/a).

At MKM, approximately 0.5 m of tailings are deposited annually, assuming they are evenly distributed across the ≈ 16.6 km^2 tailings storage facility, with historic tailings reaching depths of up to ≈ 19 m (after Wilson 2009). The total annual CO_2 equivalent emissions at MKM are reported to be 0.37 Mt CO_2 (BHP Billiton 2005). GHG emissions from mining operations are typically divided between fossil fuel combustion from distributed sources like trucks and mining equipment, and emissions from electricity generation. It is estimated that ≈ 64 % of emissions are from electricity generation, and ≈ 36 % are from distributed sources (USEPA 2008). This suggests that at MKM, approximately 0.24 Mt CO_2/year is produced from point sources. If CO_2 were injected at a rate equal to the rate of point source CO_2 emissions (≈ 328 mol CO_2/year/m^2 tailings; after BHP Billiton 2005), current brucite production rates are nearly sufficient to offset point source CO_2 emissions (fig. 1A). Higher injection rates could be initially applied to carbonate historic tailings. For instance, it would

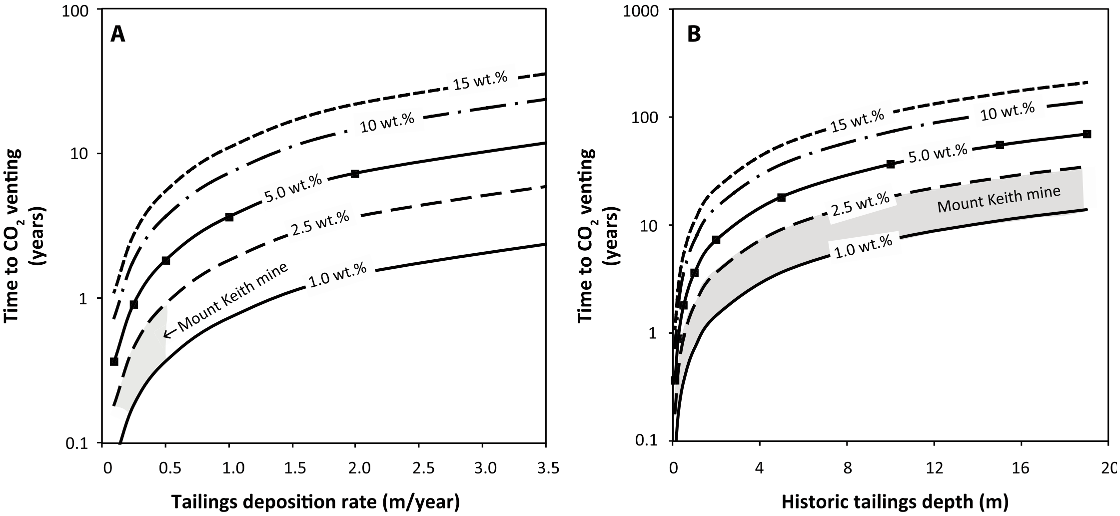

Fig. 1 *Time to CO_2 venting versus tailings deposition rate (A) and historic tailings depth (B) at various brucite contents with a CO_2 injection rate equal to the estimated rate of point source CO_2 emissions at the Mount Keith Nickel mine (≈ 238 mol CO_2/year/m^2 tailings; after BHP Billiton 2005). Shaded areas indicate range of brucite content and tailings depth and deposition rate applicable to the Mount Keith Nickel mine.*

take up to 20 years for CO_2 to vent from the deepest tailings at MKM at this CO_2 injection rate (fig. 1B). For highly reactive minerals like brucite, the reactive capacity rather than the mineral carbonation rate will likely limit the maximum CO_2 injection rate.

At mines with high tailings production rates that produce power on-site, such as MKM, it is estimated that a minimum brucite content in tailings of ≈ 3 wt. % would be required to offset point source mine emissions, or ≈ 64 % of total emissions, if brucite is the primary sink for CO_2 (figs. 1A and 2). Smaller 'off-grid' mines produce greater CO_2 emissions per tonne of tailings produced, and would require in excess of 6.5 wt. % brucite to offset estimated point source emissions (fig.2). Regardless of electricity source or mine size, accelerated carbonation of even minor amounts of brucite (*e.g.* 2.5 wt. %) could provide >4-fold acceleration over passive carbonation rates (fig. 2). In the case of a carbon tax or cap-and-trade system, offsetting GHG emissions would be financially beneficial for mining companies. Economically marginal deposits that possess significant carbon capture potential, such as high brucite content, may therefore become financially viable (*e.g.* Bobicki *et al.* 2012).

Although accelerated brucite carbonation would provide significant offsets of mine emissions, in order to take full advantage of the sequestration capacity offered by mine tailings, Mg-silicate carbonation must also be enhanced (fig. 2). Passive carbonation of serpentine has been documented in tailings with and without brucite (Wilson 2009; Wilson *et al.* 2006, 2009). This demonstrates that despite being less reactive than brucite, Mg-silicate carbonation is possible in a tailings environment. Injection of CO_2-rich gas into tailings will not only exploit the sequestration potential of brucite, but may also help carbonate the more abundant Mg-silicates. Due to the lower reactivity of Mg-silicates in comparison to brucite, more aggressive methods are often employed in mineral carbonation processes to accelerate dissolution, such as the use of strong acids (*e.g.* Alexander *et al.* 2007). Hence, it is unlikely that injection of CO_2-rich gas alone will allow sufficient acceleration of Mg-silicate carbonation to take full advantage of

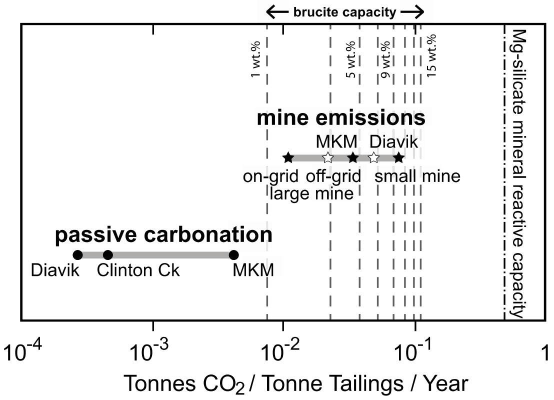

Fig. 2 *Comparison of range of passive annual carbonation rates at Diavik Diamond Mine, Northwest Territories, Canada, Clinton Creek Chrysotile mine, Yukon, Canada, and the Mount Keith Nickel Mine (MKM), Western Australia (circles) with annual GHG emissions at mine sites of various size and power sources (stars). Open and filled stars represent estimated point source and total CO_2-equivalent emissions, respectively. Total reactive capacity including Mg-silicate carbonation is indicated by the black vertical dashed-dot line. The reactive capacity per tonne tailings based on brucite carbonation alone at various brucite contents is indicated by the grey vertical dashed lines at 2 wt. % brucite intervals (modified after Harrison et al. 2013).*

the CO_2 sequestration potential. As research to enhance Mg-silicate carbonation continues, deployment of accelerated brucite carbonation strategies in the interim will help guide the development of Mg-silicate carbonation techniques for mine tailings, while providing an immediate and significant GHG benefit.

Conclusions

Experimental results indicate that passive rates of carbonation could theoretically be accelerated to offset ≈ 20-60 % of total CO_2 emissions at the Mount Keith Nickel Mine in Australia. This could be achieved via injection of CO_2-rich gas into tailings, such as flue gas from mine site power plants, to completely carbonate brucite and partially carbonate Mg-silicates. Mines that contain >6.5 wt. % brucite in their tailings may have the potential to completely offset point source CO_2 emissions via brucite carbonation alone. Carbonation of the more abundant Mg-silicates could capture >10-fold the scale of mine emissions at a large mine such as MKM. Deployment of accelerated brucite carbonation strategies would offer a first step towards the development of methods that take advantage of the total CO_2 sequestration capacity of mine tailings, while providing an immediate GHG benefit.

Acknowledgements

This research was funded by grants held by GMD from the Carbon Management Canada National Centre of Excellence and the Natural Sciences and Engineering Research Council of Canada (NSERC). IMP was funded by an NSERC Postdoctoral Fellowship. ALH was funded by a University of British Columbia Four Year Fellowship.

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