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Carbonation, Cementation, and Stabilization of Ultramafic Mine Tailings

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ABSTRACT: Tailings dam failures can cause devastation to the environment, loss of human life, and require expensive remediation. A promising approach for de-risking brucite-bearing ultramafic tailings is in situ cementation via carbon dioxide (CO₂) mineralization, which also sequesters this greenhouse gas within carbonate minerals. In cylindrical test experiments, brucite $[Mg(OH)_2]$ carbonation was accelerated by coupling organic and inorganic carbon cycling. Waste organics generated CO₂ concentrations similar to that of flue gas (up to 19%). The abundance of brucite (2–10 wt %) had the greatest influence on tailings cementation as evidenced by the increase in total inorganic carbon (TIC; +0.17–0.84%). Brucite consumption ranged



from 64–84% of its initial abundance and was mainly influenced by water availability. Higher moisture contents (e.g., 80% saturation) and finer grain sizes (e.g., clay-silt) that allowed for a better distribution of water resulted in greater brucite carbonation. Furthermore, pore clogging and surface passivation by Mg-carbonates may have slowed brucite carbonation over the 10 weeks. Unconfined compressive strengths ranged from 0.4–6.9 MPa and would be sufficient in most scenarios to adequately stabilize tailings. Our study demonstrates the potential for stabilizing brucite-bearing mine tailings through in situ cementation while sequestering CO_2 .

KEYWORDS: mining, dam failures, greenhouse gas emissions, CO_2 sequestration, CO_2 mineralization, brucite, magnesium carbonate

INTRODUCTION

Several catastrophic dam failures during the past decade have resulted in severe environmental impacts and loss of human life.¹⁻³ Consequently, there is a crucial need to develop new management practices for de-risking and safely storing mine tailings. One common cause of dam failures is the liquefaction of tailings, which can be minimized by cementing tailings with secondary mineral precipitates including carbonates that also sequester carbon dioxide (CO_2) . The net accumulation of this greenhouse gas (GHG) in the atmosphere has necessitated the development of technologies for reducing emissions^{4,5} including CO₂ mineralization that involves the reaction of powdered Ca- or Mg-rich rock with CO₂ to form carbonate minerals.^{5–10} Ultramafic (Mg-rich) mine tailings are a widely available and abundant waste product that is a valuable feedstock for CO₂ mineralization and may allow the mining industry to reduce their net GHG emissions at a relatively low cost.¹¹⁻¹³ Carbonation of Mg-silicate (e.g., serpentine) and -hydroxide (e.g., brucite) minerals found in ultramafic tailings into secondary Mg-carbonate phases may have the added benefit of physically stabilizing tailings and improving resistance to liquefaction.¹⁴ CO₂ mineralization and cementation have been documented at several mines including the Clinton Creek asbestos mine in Yukon, Canada,¹⁵ Woodsreef asbestos mine, New South Wales, Australia,¹⁶ and Mount Keith Nickel Mine in Western Australia¹⁷ (Figure S1 in the

Supporting Information). However, cementation at these mines is generally in localized areas and occurred unintentionally over long periods (e.g., years to 10s of years), whereas a deliberate and accelerated process is needed to develop carbonation as a management practice for stabilizing ultramafic tailings.

Brucite $[Mg(OH)_2]$, a common minor constituent of ultramafic tailings,^{12,17,18} exhibits fast dissolution rates relative to silicate minerals [e.g., serpentine; $Mg_3Si_2O_5(OH)_4]^{7,12,14,18-26}$ and has high reactive surface areas,²⁷ thereby facilitating rapid carbonation when exposed to CO_2 . Previous studies investigating carbonation of brucite-bearing materials have shown that grain size,^{12,15,28,29} moisture content,^{28,30,31} and brucite abundance^{12,31,32} are important variables in determining carbonation potential; however, CO_2 supply is the rate-limiting process for brucite carbonation at ambient temperature and pressure.^{12,17,21,27,28,33-36} Increasing the supply of CO_2 using elevated concentrations of CO_2 gas,³⁴ higher flow rates,³⁵ and enhancing the rate of CO_2 hydration³⁶

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Table 1. Mixtures for the Cylinders Used in the Brucite, Moisture, Grain Size, and Time Series Experiments^a

series	cylinder ID $(n = 3)$	grain size (µm)	brucite ore abundance (wt %)	water saturation (%)	porosity (%)	average TIC change (%)	average strength (MPa)
brucite abundance	B2M60VFS	63-125	2	58	43	0.17	0.5 ± 0.1
	B6M60VFS	63-125	6	58	47	0.48	3.3 ± 0.6
	B10M60VFS	63-125	10	59	44	0.87	6.9 ± 0.5
	B6M40VFS	63-125	6	39	43	0.49	2.2 ± 0.5
moisture	B6M60VFS	63-125	6	60	41	0.53	2.8 ± 0.8
	B6M80VFS	63-125	6	80	41	0.60	4.0 ± 0.5
	B6M60CS	<63	6	59	46	0.59	0.4 ± 0.1
grain size	B6M60VFS	63-125	6	58	43	0.50	3.0 ± 0.7
	B6M60FS	125-250	6	59	41	0.48	3.6 ± 0.5
time	B10M60VFS (1–9 weeks)	63-125	10	61	42	n/a	n/a

"Grain sizes included: fine (125–250 μ m), very fine (63–125 μ m), and clay-silt (<63 μ m) serpentinite. Moisture content and porosities are averages of the triplicates.

have been shown to accelerate brucite carbonation in batch slurry experiments. Although CO_2 -rich gases (e.g., flue gas) can be used for rapid carbonation of brucite,¹² these are not always readily available at mines with brucite-bearing tailings and would require infrastructure for injection into tailings impoundments.

Microbial respiration of organics may offer an alternative source of CO_2 to the atmosphere or industrial point sources. Organic and microbial amendments such as peat,³⁷ filamentous cyanobacteria,^{38,39} and heterotrophic bacteria⁴⁰ have been applied to mine tailings for remediation or to enhance CO₂ mineralization. The addition of organics to tailings leads to elevated alkalinity and dissolved carbon concentrations in pore waters, thereby promoting carbonate precipitation.^{38,40,41} Furthermore, ultramafic asbestos tailings that were inoculated by a consortium dominated by cyanobacteria promoted in situ cementation of fibrous chrysotile, thereby solidifying and stabilizing the tailings.³⁸ Microbially induced carbonate precipitation has also been shown to be an effective means of cementing materials for the purpose of construction and stabilizing aggregates.^{42,43} Yet, accelerating mineral carbonation through organic amendments for the purpose of mine tailings stabilization and CO₂ sequestration has not previously been investigated.

Here, we propose coupling organic and inorganic carbon cycling to accelerate brucite carbonation within ultramafic tailings for stabilization and CO₂ sequestration. This study aimed to elucidate the controls on brucite carbonation when reacted with CO2 generated from waste organics and assess tailings stabilization after the formation of secondary carbonate cement. Cylindrical text experiments simulated the storage conditions of unsaturated brucite-bearing ultramafic tailings that have been amended with organics. In these experiments, we examined the effects of brucite abundance, moisture content, particle size, and reaction time on secondary carbonate cement formation, which was assessed using inorganic carbon and unconfined compressive strength analyses. This study has broad implications for stabilizing and de-risking tailings storage impoundments by facilitating geochemical reactions that form cement at the pore scale.

MATERIALS AND METHODS

Carbonation experiments were used to investigate the influence of brucite $[Mg(OH)_2]$ abundance, moisture content, grain size, and reaction time on CO_2 mineralization and

cementation of brucite-bearing synthetic mine tailings (Table 1). Serpentinite from the Lizard Ophiolite, United Kingdom, was crushed with a hammer (<1.6 cm), pulverized (FLSmidth Essa LM2 Pulverizing Mill), and sieved to specific size fractions (<63 μ m, 63–125 μ m, and 125–250 μ m). Brucite ore from Nevada, United States, was pulverized resulting in a bimodal distribution centered on 0.2 and 5.9 μ m (Figure S2). The brucite used in experiments was sourced from the same batch as the one used by Harrison et al.^{21,27,28,34} and Power et al.³⁵ X-ray diffraction analysis of the brucite ore determined that it contained 73.5 wt % brucite and also hydromagnesite (16.0 wt %), dolomite (4.1 wt %), magnesite (3.2 wt %), chrysotile (2.5 wt %), and pyroaurite (0.7 wt %; Table S1). The serpentinite was composed of 95.2 wt % lizardite [Mg₃Si₂O₅(OH)₄] and 2.4 wt % each of forsterite and hematite. The MgO abundances of the brucite ore and serpentinite were 62.9 and 37.7%, respectively, as determined by X-ray fluorescence spectroscopy (XRF; Table S2). For comparison, the MgO contents of pure brucite and serpentine are 69.1 and 43.6% based on their ideal formulas, respectively.

Cylindrical test specimens (2.5 cm diameter; 5.0 ± 0.1 cm height) were prepared using various mixtures of pulverized serpentinite and brucite ore to simulate compacted brucitebearing ultramafic tailings (Table 1). Similar tailings are produced at the Mount Keith Nickel Mine (avg. ≈2.5 wt % brucite)¹⁷ and Black Lake in Thetford Mines, Québec, Canada (<3.6–5.1 wt % brucite),⁴⁴ and prospective tailings may be produced from the Baptiste nickel deposit in British Columbia, Canada (0 to >10 wt % brucite).^{12,23} Mixtures were homogenized in 1 L plastic jars. Aliquots ($\sim 2-4$ g) of synthetic tailings were layered into acrylic cylindrical molds (2.54 cm diameter), compacted with a tamper, and wetted by dropwise addition of deionized water equilibrated with atmospheric CO₂ (pH \sim 5.6). Once a layer was wet, an additional aliquot of tailings was added. Tailings were repeatedly layered until the cylinder reached a height (5.1 cm) that was approximately equal to twice the diameter. This method ensured that water was equally distributed throughout the cylinder. Triplicates were made and kept in their molds that were wrapped with parafilm to minimize evaporation prior to being removed using the tamper and placed in chambers (Figure S3).

The effect of brucite abundance on tailings cementation was tested using cylinders with 2, 6, and 10 wt % brucite, all of which contained very fine sand-sized serpentinite (63–125 μ m) and 60% moisture (Table 1). Very fine sand-sized



Figure 1. CO_2 concentrations (%) versus time (days) for chambers containing cylinders with varying (a) brucite abundance, (b) moisture content, (c) grain size, and (d) reaction time. The square markers in the reaction time series indicate when a cylinder was removed from its chamber.

serpentinite with 6 wt % brucite was used to test the effect of moisture content using cylinders with 40, 60, and 80% water as a percent of pore space. The relative humidity of the air within the chambers was likely 100% given that water droplets formed on the lids. Cylinders for the grain size experiment used claysilt (<63 μ m), very fine sand (63–125 μ m), and fine sand $(125-250 \ \mu m)$ sized serpentinite and contained 6 wt % brucite and 60% moisture (particle size distributions are in Figure S2). Although the grain size of ultramafic tailings is generally <63 μ m,^{12,17,40} particle size distributions can vary among different mines. The specific surface areas of these three grain sizes were 33.0, 31.5, and 30.7 m²/g, respectively, as determined by the N_2 adsorption method. Finally, a mixture of very fine sand-sized serpentinite, 10 wt % brucite, and 60% moisture was used in a time series experiment (9 weeks) with cylinders being sampled each week.

Triplicate cylinders were placed on porous stainless-steel discs (3.81 cm in diameter; 1.6 mm thick; 40 μ m) inside 3 L plastic containers with Tygon tubing and a valve on the side (Figures S3 and S4). The discs allowed for the bottom of each cylinder to be exposed to air. Compost from Trent University's Experimental Farm (C/N = 10.8; Table S3) was used as an organic source of CO₂ for reaction with brucite; however, any CO₂-generating waste organic is expected to serve the same purpose. Large pieces of organic matter (e.g., twigs) and rocks were removed by hand before it was dried for 2 days and passed through a 5.66 mm (#3.5) sieve. Compost moisture content was determined through experimentation and measured with a TEROS 10 soil moisture sensor (METER

Group, Inc. USA). An ideal moisture content of \sim 40% was found for mixtures of 350 g of dried compost with 450 mL of deionized water. The compost was added to the chambers that were sealed with rubber-rimmed lids to ensure an airtight space. The compost was analyzed for its total carbon and nitrogen contents, populations of aerobic and anaerobic heterotrophic bacteria, and carbon substrate utilization.

With the exception of the time series experiment, cylinders remained in the chambers for 10 weeks under laboratory temperature (~22 °C). CO_2 concentrations in each chamber were measured at a time interval of 30 min or 1 h for the first 7 h to track the expected rapid initial increase. In subsequent days, CO_2 concentrations were measured daily until the completion of the experiment. For the time series experiment, measurements were also done before and after a cylinder was removed from its chamber. A control chamber with only compost was used in each of the experiments to measure CO_2 concentrations in the absence of the cylinders. Additional controls were used to measure oxygen (O_2) depletion during the experiments and CO_2 generation under anaerobic conditions.

Reacted cylinders were tested for their unconfined compressive strengths (UCS) after being dried under laboratory conditions until each cylinder had a consistent mass. This approach was chosen to ensure more reproducible UCS measurements among the triplicate cylinders. Fragments of the cylinders were imaged using scanning electron microscopy (SEM) with elemental analysis by energydispersive spectroscopy. The mineralogical composition of

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the cylinders was determined using powdered X-ray diffraction (XRD), and total inorganic carbon (TIC) was measured using coulometry. Details of the analytical methods are provided in the Supporting Information.

RESULTS AND DISCUSSION

CO₂ Supplied by Organics. Stable isotopic data of secondary Mg-carbonate minerals formed in the ultramafic tailings at the Mount Keith Nickel Mine showed that brucite carbonation was limited by the ingress CO₂ from the atmosphere into tailings.¹⁷ Furthermore, the carbonation of slurries containing very fine-grained (<53 μ m) brucite, similar to that used in this study, was also limited by CO₂ supply even when using 10% CO_2 gas.³⁴ In the present study, the supply of CO₂ was dramatically increased with the use of organic-rich compost (27% C). The water-to-compost ratio of approximatley 1.3 (\sim 40% moisture) and the low C/N ratio (11–12) favored microbial respiration and the production of CO₂ gas.^{45,46} Microbial populations of aerobic and anaerobic heterotrophic bacteria were 2.1×10^7 and 9.0×10^6 colonyforming units (cfu)/g, respectively. Heterotrophic bacteria respired organics [e.g., glucose $(C_6H_{12}O_6)$] in the compost via aerobic and anaerobic pathways to release CO₂ and other gases (eqs 1 and 2 are example reactions).

Aerobic respiration: $C_6H_{12}O_6 + 6O_2$

$$\rightarrow 6CO_{2(g)} + 6H_2O + Energy (heat)$$
 (1)

Anaerobic respiration: 2. $5C_6H_{12}O_6 + 12NO_3^{-1}$

$$\rightarrow 6N_2 + 15CO_{2(g)} + 12OH^- + 9H_2O + Energy ($$

heat) (2)

The microbial consortium in the compost utilized a wide range of carbon substrates as determined using Biolog EcoPlates (Figure S5). CO_2 concentrations in the controls increased linearly $(R^2 = 0.98)$ at an average rate of 0.48% (4800 ppm)/h for the first 8 h and continued to rise in the three control chambers reaching maximums of 13-19% with most of this CO_2 being generated in the first week (Figure 1). The chambers became anoxic with the O_2 concentration being reduced to below detection in a control chamber after 2 days (Figure S6a). CO_2 production was ~0.03%/h during the first week of measurements in a control that was set up under anaerobic conditions (Figure S6b). Thus, CO₂ production remained substantial during experiments even after O₂ became depleted (eq 2). Simultaneously, the production of other gases $\frac{1}{2}$ (e.g., CH_4 and N_2O) in the sealed chambers would have diluted CO₂ and may also have interfered with measurements by the nondispersive infrared CO₂ sensors that are crosssensitive with CO_2 and CH_4 . As a result, the decrease in CO_2 concentration in all control chambers toward the end of the experiments is likely attributed to anoxic conditions. Nevertheless, CO_2 concentrations in the controls were generally held at >10% for the duration of the experiments.

The CO₂ concentrations achieved in experiments rival that of flue gas (8-15%),⁴⁷ which has been proposed as a CO₂ point source for the carbonation of serpentinites.⁴⁸ With regards to brucite, its carbonation has been shown to increase by 240-fold using 10% CO₂ gas compared to controls that used atmospheric CO₂.³⁴ In mining environments, amending tailings with waste organics for remediation purposes leads to elevated alkalinity and CO₂, findings that were supported by decreasing δ^{13} C values of the dissolved organic carbon toward isotopic values of the bulk organic sources.³⁷ Although other factors influence the rate and extent of brucite carbonation, the high CO₂ concentrations achieved in the experiments acted to greatly accelerate this process, thereby demonstrating the efficacy of using this alternative CO₂ source.

Controls on Brucite Carbonation. Brucite abundance had a clear effect on CO_2 concentrations due its ability to rapidly react with this GHG. Microbial respiration of the compost generated CO_2 (eqs 1 and 2) that would have dissolved into pore waters and hydrated (e.g., HCO_3^- ; eq 3), while brucite readily dissolved^{22,49} and released Mg²⁺ to form hydrated Mg-carbonate minerals (e.g., dypingite; eq 4).

$$\operatorname{CO}_{2(g)} \rightleftharpoons \operatorname{CO}_{2(aq)} + \operatorname{H}_2 \operatorname{O} \rightleftharpoons \operatorname{H}_2 \operatorname{CO}_3 \rightleftharpoons \operatorname{HCO}_3^- + \operatorname{H}^+$$
(3)

$$5Mg(OH)_2 + 4H^+ + 4HCO_3^-$$

 $\rightarrow Mg_5(CO_3)_4(OH)_2 \sim 5H_2O + 3H_2O$ (4)

This coupling of organic and inorganic carbon cycling is an effective approach to accelerate in situ brucite carbonation. The concentration of CO₂ in the chamber with the 2 wt % brucite cylinders increased logarithmically. The maximum concentration of 7% was reached in 12 days and stabilized until 30 days, after which CO₂ concentrations slightly decreased (Figure 1a). For comparison, the 6 and 10 wt % brucite chambers reached only 1 and 0.1% CO₂ by approximately 12 days. The increases in TIC for the 2, 6, and 10 wt % brucite cylinders averaged 0.17, 0.48, and 0.83% C, respectively, which support CO₂ measurements. XRD results from the experiments showed that brucite abundance decreased from initial values in all experiments but was not completely consumed (Figures S7 and S8). Furthermore, there was no clear trend between brucite consumption and its initial abundance with 68, 78, and 71% of the 2, 6, and 10 wt % brucite being carbonated, respectively (Figure 2). This finding indicates that neither CO_2 nor water limited carbonation. Note that the 2 and 10 wt % brucite cylinders had the same moisture content and were exposed to similar CO₂ concentrations, yet the former did not achieve complete carbonation (68%).



Figure 2. Average increase (final – initial) in total inorganic carbon (%C) versus brucite carbonation given as a percentage of the amount of brucite carbonated/consumed (e.g., complete brucite carbonation = 100%). The brucite abundance, moisture content, grain size, and time series experiments are plotted.



Figure 3. Representative back-scattered electron micrographs of a cylinder (very fine serpentinite, 6 wt % brucite, and 60% moisture) after experimentation and embedment in epoxy. (a) Serpentinite (serp.) grains cemented by Mg-carbonate with a flakey morphology indicative of dypingite and hydromagnesite. (b) Large brucite grain (~200 μ m) that was passivated by a thick rind (~50 μ m) of Mg-carbonate. Mineral identifications were based on energy-dispersive spectroscopy and prior knowledge of the mineralogical compositions from X-ray diffraction analysis. Black areas are epoxy that has infilled pore spaces.

Initial CO₂ concentrations within the chambers of the moisture series ranged from 0.06% to 0.11% and increased rapidly during day 1 followed by a rapid decline in day 2 (Figure 1b). This pattern of a spike in CO_2 concentration during the first 2 days was most clearly observed in the moisture series yet was also seen in some other experiments. Similar patterns in Mg and dissolved inorganic carbon concentrations were noted during carbonation of brucite slurries with CO2-rich gases and were attributed to the induction time (i.e., time for nucleation) for Mg-carbonate precipitation.^{34,35} In other words, a delay in forming Mgcarbonates during the first day allowed for the rapid increase in CO₂, which was then partly consumed once Mg-carbonate precipitation began. The CO₂ concentration rose more rapidly in chambers with the 40% moisture cylinders. However, similar CO₂ levels were measured for all chambers of the moisture series after approximately 35 days, which was likely due to decreasing carbonation rates as brucite became depleted. The fluctuating CO₂ concentrations after \sim 50 days (Figure 1b) and most notable in the moisture series experiment were likely due to measurement interference by other gases (e.g., CH_4) as the chambers became anoxic.

Carbonation of brucite-bearing ultramafic tailings can be enhanced by optimizing water availability as it is needed for mineral dissolution, CO₂ hydration, and carbonate precipitation;^{11,28} however, greater amounts of water in pore spaces may also reduce permeability and limit CO₂ supply. Optimizing brucite carbonation rates has been achieved with water contents of between 40 and 60%.^{21,28,31,50} In contrast, increasing water content within the cylinders resulted in greater brucite carbonation with the 40, 60, and 80% moisture cylinders exhibiting increases of 0.49, 0.53, and 0.60% C, respectively (Figure 2). Consequently, there was a clear relationship between the moisture content and brucite consumption with the 80% moisture cylinders having 84% of the initial brucite being reacted. Gravimetric measurements of the initial (moist) and final (dried) cylinders showed that only 5% (40% cylinders) to 9% (80% cylinders) of the initial bulk water was consumed, suggesting that there should have been sufficient water for carbonation reactions. Harrison et al.²⁸ demonstrated that the majority of water loss during brucite carbonation in column experiments could be attributed to incorporation into hydrated Mg-carbonate minerals; this was likely the case in this study given that the air in the chambers was saturated to prevent evaporation. The authors emphasized the importance of water availability including its distribution at

the pore scale, which can be heterogeneous. Microfluidics experiments that visualized brucite carbonation at the pore scale further demonstrated the importance of water availability (wet versus dry pores) and its control on reaction rates.²⁷ As such, there may have been water limitations at the pore scale where substantial hydrated Mg-carbonate formation consumed water. Thus, cylinders with a greater bulk water content (e.g., 80%) also likely had greater water availability in pores for brucite dissolution and carbonate formation.

Cylinders composed of clay-silt-sized (<63 μ m) serpentinite showed a similar, yet slower increase in CO₂ concentration compared to the control, reaching 12% by 9 days (Figure 1c). Note that the brucite used in all cylinders had the same grain size (see the Supporting Information for particle size distributions). Although CO₂ concentrations fluctuated, there was a slight decline to 6-7% by the end of the experiment that again likely related to chambers becoming anoxic. The cylinders composed of very fine $(63-125 \ \mu m)$ and fine (125–250 μ m) serpentinite exhibited slower increases in CO₂ concentration reaching maximums of 8.8 and 10.7% by 41 and 36 days, respectively. The initially higher concentration of CO_2 in the chamber with the clay-silt cylinders is likely explained by the lower permeability as a result of the finer grain size compared to fine and very fine serpentinite, which may have slowed the overall rate of carbonation due to slower rates of CO_2 ingress into the cylinders (Figure 1c). For the cylinders containing fine, very fine, and clay-silt serpentinite, the TIC contents increased by 0.48, 0.50, and 0.59% C, respectively. Brucite consumption for the three grain sizes was 64% (fine sand), 76% (very fine sand), and 83% (clay-silt) of the initial 6 wt % brucite (Figure 2). These data demonstrate that although the carbonation rate may have been slower in the clay-silt cylinders, the extent of carbonation was greater. Consequently, the concentration of CO_2 in the chambers may more so reflect the rates of CO_2 consumption rather than the extent of brucite carbonation. In other words, the lower permeability of the claysilt cylinders may have negatively impacted the rate of CO₂ ingress; however, the long reaction times (10 weeks) and high CO₂ concentrations appear to have counteracted this impedment.¹⁷ In fact, the clay-silt cylinders exhibited the greatest brucite carbonation (83% consumption) of the three grain sizes, matching that of the 80% moisture cylinders (84% consumption). One possibility is that the finer clay-silt serpentinite with greater capillary forces enhanced water distribution, thereby allowing water to more easily move to pores where it was being consumed by hydrated Mg-carbonate

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Figure 4. Unconfined compressive strengths (UCS) of cylinders. (a) UCS and total inorganic carbon of the cylinders in the time series. (b) Average (n = 3) strength of the cylinders with varying brucite abundance, moisture content, and serpentinite grain size. Note that there were nine replicates for cylinders containing 6 wt % brucite and 60% moisture and using very fine serpentinite (Table 1).

precipitation. Furthermore, the larger grain sizes (e.g., fine sand) would have larger pores that when wetted are the last to fill with water. If these larger pores contained brucite, then there may have been insufficient water for carbonation. This finding supports the importance of not only water abundance but also its availability and distribution within a porous medium.^{21,28}

The time series experiment used cylinders with 10 wt % brucite, which greatly suppressed CO_2 concentrations (e.g., <1% for the first 3 weeks). An initial increase was followed by a decrease in the first 2 days and was attributed to a delay in Mgcarbonate precipitation (Figure 1d). CO₂ concentrations increased in the chamber containing the cylinders that were sampled on weeks 1, 2, and 3. Although opening the chamber caused a sudden decrease in CO₂, its concentration rapidly recovered and further increased. This pattern was noted for each of the three chambers as removing a cylinder also equates to removing CO₂-consuming brucite, as well as replenishing the chamber with O_2 that promoted CO_2 generation from compost. The chamber from which cylinders were sampled at 7, 8, and 9 weeks showed a similar trend in CO_2 concentrations, remaining at <1% for the first 3 weeks and then increasing to 5% by the end of the experiment (Figure 1d). Longer reaction times resulted in greater carbonation; however, the rate slowed as evidenced by the TIC data (Figure 2). Brucite consumption reached 69% by 49 days and only increased to 71% by 63 days, similar to that of the 10 wt % cylinders (71% consumption) that were reacted for 70 days. The slowing of brucite carbonation indicates that CO₂ ingress into the cylinders may have been hindered due to clogging of pore spaces and surface passivation.

Examination of polished embedded samples showed extensive infilling (clogging) of pores (Figure 3a) and passivation of larger brucite grains (e.g., ~200 μ m) that developed thick rinds (~50 μ m) of Mg-carbonate (Figure 3b). Surface passivation of reacting minerals by secondary precipitates may result from coupled dissolution—precipitation reactions, including brucite carbonation, that occurs at the mineral—fluid interface.^{17,28–30,51–53} In addition, there is a volume increase when converting brucite (molar volume = 24 cm³/mol) to a Mg-carbonate mineral such as dypingite (404%). Harrison et al.²⁸ postulated that pervasive coatings on mineral surfaces and passivation of brucite grains by

carbonate rinds (10-100 s of microns) limit brucite carbonation. The slowing rate of TIC increase (Figure 4a) and the lack of a correlation between brucite abundance and consumption (Figure 2), as previously discussed, suggest that pore clogging and surface passivation limited brucite carbonation.

CO₂ Sequestration within Mine Tailings. Unintentional passive carbonation and cementation of brucite-bearing ultramafic tailings have been documented at the Mount Keith Nickel Mine (Figure S1; most cemented tailings were 8 years old),¹⁷ Woodsreef asbestos mine, New South Wales, Australia (closed in 1983),⁵⁴ and the Clinton Creek asbestos mine (closed in 1978).¹⁵ While these tailings are primarily comprised of serpentine group minerals $[Mg_3Si_2O_5(OH)_4]$, the presence of highly reactive brucite substantially enhances their overall CO₂ sequestration potential.⁵⁵ In experiments, brucite carbonation resulted in millimeter-scale efflorescences on cylinder surfaces (Figures S9 and S10). Compared to unreacted tailings, XRD patterns of reacted cylinders (Figure (\$8) showed an increase in the intensity of a peak at 17.6° 2θ (CuK α), which indicated an increase in dypingite and/or hydromagnesite $[Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O]$. Note that the brucite used in experiments contained 16 wt % hydromagnesite. These XRD results were corroborated by observations by SEM that showed poorly crystalline, flakey Mg-carbonate, a morphology common of dypingite and hydromagnesite (Figures 3a and S11).^{56,57} The formation of these minerals in the cylinders is consistent with those cementing tailings at the aforementioned mines. Carbonation of brucite within ultramafic tailings may also produce poorly crystalline or amorphous phases that cannot be quantified by XRD.¹² Newly formed carbonate, whether amorphous or crystalline, is best quantified by TIC measurements, as was done in this study and in others, which provide greater accuracy.^{12,54}

In the case of CO₂-limited brucite carbonation, the mineral sinks for CO₂ have been shown to shift away from hydrated Mg-carbonate minerals to hydrotalcite minerals such as coalingite $[Mg_{10}Fe^{3+}_2(CO_3)(OH)_{24}:2H_2O]$ and pyroaurite $[Mg_6Fe^{3+}_2(CO_3)(OH)_{16}:4H_2O]$ as observed in deeper tailings at the Woodsreef mine.^{16,54} This CO₂ limitation could be overcome by using organic amendments on tailings, thereby coupling organic and inorganic carbon cycling. For instance,

 $\rm CO_2$ generated from waste organics that were discharged into the impoundment at the Diavik Diamond Mine (Northwest Territories, Canada) was partly sequestered in carbonates as evidenced by stable carbon and oxygen isotope data that can discriminate carbon sources, e.g., organic carbon versus atmospheric $\rm CO_2$.⁵⁸ CO₂ mineralization using organics as an alternative source of CO₂ would be considered GHG emission avoidance if it can be demonstrated that the CO₂ would have otherwise been released to the atmosphere.

Carbonation of reactive brucite within mine wastes has the potential to render certain mines carbon neutral. For example, Vanderzee et al.²³ estimated that the Baptiste nickel deposit, composed mainly of serpentinite, has an average of 2.3 wt % labile MgO, which they defined as magnesium sourced from brucite (present at 0 to >10 wt %) and serpentine surfaces. Brucite carbonation in our experiments ranged from 64-84% consumption in cylinders exposed to CO₂ generated from organics for 10 weeks (Figure 2). The overall amount of brucite carbonation in experiments was mainly controlled by the initial brucite abundance and water availability. For comparison, carbonation of only 57% of the labile MgO in the Baptiste deposit would be sufficient to completely offset mine truck emissions (11.4 t CO_2/kt rock mined), thereby making this prospective mine carbon-neutral if operated using hydroelectric power. Carbonation could be achieved using atmospheric CO₂ or a point source of CO₂; however, brucite carbonation may be limited when using the former and the use of concentrated CO₂ streams would require both a source and infrastructure for injection.¹² Although a sizable source of waste organics would need to be accessible and introduced into mine tailings, the carbonation process occurs passively without ongoing intervention.

Tailings Stabilization. While the ability of ultramafic mine wastes to sequester CO₂ is of interest to the mining industry,^{12,17,25,55,59,60} the potential hazards associated with tailings storage remain a top priority. Numerous tailings dam failures have occurred in recent years including those at the Mount Polley (Canada, 2014),⁶¹ Germano (Brazil, 2015),⁶² Córrego de Feijão (Brazil, 2019),63 and Cadia (Australia, 2018) mines and there remains serious risk of future failures. There are various approaches to stabilizing tailings including encouraging hardpan formation,^{64–71} revegetation,⁷² and paste backfill.⁷³⁻⁷⁵ For example, hardpan formation within the shallow tailings of the Nickel Rim Mine (Sudbury, Canada) in conjunction with a revegetation program aided in chemically stabilizing the tailings.^{68,71} Characterized primarily by pyrrhotite (>98%), the tailings became cemented by the precipitation of goethite and jarosite within pore spaces. Revegetation has also been historically used to reduce wind erosion and physically stabilize tailings at the Copper Cliff Mine in Sudbury, Canada.⁷² Engineered hardpans are an example of facilitating geochemical reactions and secondary mineral precipitation to cement and successfully improve the physical and chemical stability of tailings impoundments.⁶⁵ If implemented at the mine scale, carbonation may have similar positive outcomes in terms of physical stabilization and immobilization of metals being released by tailings.^{70,7}

The UCS of the cylinders was positively correlated with brucite abundance, moisture content, and reaction time (Figure 4). Brucite abundance had the greatest effect on strength with average values of 0.5 ± 0.1 , 3.3 ± 0.6 , and 6.9 ± 0.5 MPa for the cylinders with 2, 6, and 10 wt % brucite, respectively (Figure 4b). For the moisture series, an average

strength of 4.0 ± 0.5 MPa was achieved in the 80% moisture cylinders, thereby confirming that greater water availability enhanced interstitial cement formation and strength development. The 40 and 60% moisture cylinders had average strengths of 2.2 \pm 0.5 and 2.8 \pm 0.8 MPa, respectively. The cylinders with clay-silt serpentinite yielded an average strength of only 0.4 \pm 0.1 MPa, considerably less than those achieved using very fine $(3.0 \pm 0.7 \text{ MPa})$ and fine serpentinite $(3.7 \pm$ 0.5 MPa). The clay-silt cylinders developed numerous fine, horizonal fractures (Figure S9) likely due to volume changes that substantially reduced the strength of these cylinders despite greater increases in TIC (+0.59%) compared to the other grain sizes. No fractures were noted in any of the other cylinders. Expansion is less likely to cause fracturing in tailings that are under a confining pressure as would be the case in a real-world impoundment. Clay-silt cylinders had less porosity (41%) than the very fine (43%) and fine serpentinite (46%)cylinders. As previously discussed, Mg-carbonate formation within pore spaces results in expansion with the loss of pore space ranging from 2-15% in mildly to heavily cemented tailings (e.g., 2 versus 10 wt % brucite cylinders). This reduction in porosity is based on precipitation of solid dypingite (density = 2.15 g/cm^3) that lacks any of its own porosity; however, microscopy revealed that precipitates were flakey and contained considerable porosity (Figure 3a). This crystal morphology may or may not be advantageous for tailings stabilization. Similarly, dense dypingite/hydromagnesite agglomerates with a rosette-like morphology that resulted from brucite carbonation have been shown to enhance the mechanical performance of MgO cement.⁷

There was a linear correlation between the UCS and the increase in TIC (final – initial; $R^2 = 0.87$; eq 5).

$$UCS (MPa) = 9.5 \times TIC \text{ increase } (\%) - 1.6$$
(5)

The clay-silt serpentinite and time series cylinders were not included in this relationship as the former developed cracks and the latter had less time for carbonation. Regarding the time series, cylinders reached a strength of 4.8 MPa in 1 week and increased further in a somewhat linear trend through to week 6 (6.2 MPa; Figure 4a). There was a substantial and unexplained strength increase in weeks 7 (8.2 MPa) and 8 (9.6 MPa); however, the strength measurement at week 9 (6.7 MPa) was consistent with the aforementioned trend. Cylinders exhibiting the greatest increase in TIC, such as the 80% moisture (+0.60% C) and 10 wt % brucite (+0.83% C) cylinders, had notably greater compressive strengths than other cylinders in their respective series (Figure 4b), suggesting that optimizing secondary Mg-carbonate cement formation leads to micro-structure densification.^{73,79,80} Similar findings were obtained by Vanderzee et al.¹⁴ who performed experiments to carbonate prospective tailings from the Baptiste nickel deposit using 10% CO₂ gas and Yi et al.⁷⁹ who reacted brucite-bearing magnesia (MgO). For comparison, Vanderzee et al.¹⁴ achieved a UCS of 4.9 MPa for a serpentinite cylinder with 10 wt % brucite (6.8 wt % was consumed) after exposure to 10% CO₂ for 3 weeks. In this study, a 10 wt % brucite cylinder had an UCS of 4.5 MPa after 3 weeks (Figure 4a). The difference in these approaches is that the former requires a point source of CO₂rich gas (e.g., flue gas) and its injection into tailings, whereas the latter requires amending tailings with organics that generate CO₂ in situ via microbial respiration.

The minimum UCS required for impoundment stabilization is \sim 100 s kPa (e.g., 345 kPa), while free-standing paste backfill

requires a strength of 0.15-1.0 MPa to prevent barricade collapse and liquefaction.⁸¹⁻⁸⁴ Specimens in this study exhibited excellent mechanical performance, meeting or greatly exceeding these requirements and strengths obtained in various base-metal paste backfill studies (0.06-8.8 MPa).^{82,85-89} Despite differences in the rheological behavior of solid and paste backfill, these findings suggest that brucitebearing tailings can be stabilized without the need of a chemical binder (e.g., Portland cement). Furthermore, solidification-stabilization tests of tailings obtained from two base metal mines in South Korea determined that an engineered hardpan at the site improved the mechanical strength of tailings with UCS values ranging from 0.3-6.7 MPa,⁶⁵ which are similar to those achieved in this study. MgO (20 wt %), with a similar reactivity to brucite, has been shown to aid in developing high compressive strengths of 68.3 MPa due to its carbonation (0.1 MPa CO_2 , 14 days) and mixture with fly ash (20 wt %) and Portland cement.⁷³ However, in contrast to the considerable CO_2 emissions associated with Portland cement and MgO production,^{79,90,91} CO₂ mineralization of brucitebearing tailings offers the potential for stabilizing tailings while reducing net GHG emissions.

Numerous studies have investigated the addition of organics including compost, biosolids, and organic-rich sludge to tailings for the purpose of mine reclamation, technosol formation, phytostabilization, and rehabilitation.⁹²⁻⁹⁷ The addition of organics to mine tailings has also been shown to induce biogeochemical processes such as sulfate reduction, which can immobilize elements of concern (e.g., As) through the precipitation of sulfide minerals.⁹⁸ In this study, coupling organic and inorganic carbon cycling dramatically accelerated brucite carbonation, which is often limited by CO₂ supply. Waste organics offer an inexpensive CO₂ source that can be incorporated into mine wastes for in situ CO₂ generation, thereby facilitating brucite carbonation, a process that can stabilize tailings and sequester CO2. Mg-carbonate precipitation within pores resulted in considerable strength development that may have a positive effect on the stability of mine tailings if this process can be implemented at the mine scale. Although CO₂ emissions from compost are not considered in global warming accounting, the CH₄ and N₂O emissions from compost can have a negative impact.⁴⁶ Further research is needed to test these research findings at a larger scale under real-world conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c01570.

> Detailed descriptions of the analytical techniques and additional results (PDF)

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Author Contributions

I.M.P. designed the study, conducted microscopy, interpreted all data, and completed the majority of writing. C.P. assisted with experimental design, CO2 measurements, and writing as well as data collection and interpretation. H.L. set up and monitored the experiments and completed laboratory analyses. J.A.L. contributed to background research, microscopy, and writing. A.R.S. completed carbon and particle size analyses. D.F. and R.C. carried out unconfined compressive strength tests on the cylinders. All authors commented on and approved the manuscript.

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Notes

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