Bioleaching of Ultramafic Tailings by Acidithiobacillus spp. for CO₂ Sequestration

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Bioleaching experiments using various acid-generating substances, i.e., metal sulfides and elemental sulfur, were conducted to demonstrate the accelerated dissolution of chrysotile tailings collected from an asbestos mine near Clinton Creek. Yukon, Canada. Columns, possessing an acid-generating substance colonized with Acidithiobacillus sp., produced leachates with magnesium concentrations that were an order of magnitude greater than mine site waters or control column leachates. In addition, chrysotile tailings were efficient at neutralizing acidity, which resulted in the immobilization of metals (Fe, Cu, Zn) associated with the metal sulfide mine tailings that were used to generate acid. This suggests that tailings from acid mine drainage environments may be utilized to enhance chrysotile dissolution without polluting "downstream" ecosystems. These results demonstrate that the addition of an acidgenerating substance in conjunction with a microbial catalyst can significantly enhance the release of magnesium ions, which are then available for the precipitation of carbonate minerals. This process, as part of a carbon dioxide sequestration program, has implications for reducing net greenhouse gas emissions in the mining industry.

Introduction

There is strong consensus that the anthropogenic release of greenhouse gases is resulting in global climate change. One means of reducing these emissions is to sequester carbon dioxide (CO₂) in a geological medium. The formation of carbonate minerals is the most geologically stable and environmentally safe manner to store carbon (1, 2). Because ultramafic rocks have high abundances of magnesium oxide (up to 50% by weight) they are considered to be the best feedstock for mineral carbonation (3). During weathering, magnesium silicate minerals (e.g., serpentine) undergo an exothermic reaction (eq 1) to form stable magnesium carbonate minerals (4).

 $Mg_{3}Si_{2}O_{5}(OH_{4}) + 3CO_{2} \rightarrow 3MgCO_{3} + 2SiO_{2}$ $\Delta G^{\circ}_{f} = -67 \text{ kJ/mol} \quad (1)$

In fact, natural silicate weathering on Earth sequesters approximately 100 Mt of carbon each year (5). Research relating to mineral carbonation has generally involved the conversion of magnesium silicate minerals to form magnesite (MgCO₃) via chemical treatment under high pressure and temperature (1, 6). However, the large amount of energy required for mining and processing may not allow CO₂ sequestration to be economically feasible by this means (7). In order to reduce costs, the use of waste chrysotile asbestos has been suggested as one possible feedstock for mineral carbonation (7, 8). This has the added benefits of eliminating the costs of mining and utilizing a hazardous waste product.

Wilson et al. (2, 9) documented the passive formation of secondary magnesium carbonate minerals within chrysotile tailings at abandoned asbestos mines near Clinton Creek, Yukon, and Cassiar, British Columbia, Canada. The high surface area and exposure of the tailings at the Earth's surface has made them amenable to mineral carbonation. Using quantitative techniques, these authors determined that 164 kt of CO_2 has been sequestered in the Clinton Creek tailings pile. However, there is still enormous potential for further carbon sequestration in these tailings. Complete carbonation of the 10 Mt of chrysotile tailings to form hydromagnesite, the dominant secondary carbonate (2), would sequester approximately 3.8 Mt of CO_2 (eq 2).

$$5Mg_{3}Si_{2}O_{5}(OH)_{4} + 5H_{2}O + 12CO_{2} \rightarrow$$

 $3Mg_{5}(CO_{3})_{4}(OH)_{2}.4H_{2}O + 10SiO_{2}$ (2)

The dissolution of the chrysotile tailings, while enhanced by their high surface area, is the limiting factor given the slow kinetics of the proton production in the CO_2-H_2O system (4, 10). In natural environments, weathering rates are dramatically enhanced by the biological production of inorganic and organic acids in soils that overlay bedrock (11).

The tailings pile at Clinton Creek lacks any acid-generating substance (AGS) that would further enhance chrysotile dissolution. Teir et al. (10) used both inorganic and organic acids to accelerate the release of magnesium from serpentinite tailings and concluded that sulfuric acid was the most effective. As opposed to organic acids, the use of sulfuric acid does not contribute any foreign carbon. In this study, we examine the use of waste products including sulfides and elemental sulfur as sources of sulfuric acid, which can be obtained from acid mine drainage sites and desulfurization of sulfur-rich gases, respectively. To increase acid generation, we have utilized *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* to accelerate oxidation of these AGS.

Column leaching experiments were conducted in two phases (month and year long trials) to demonstrate biologically catalyzed oxidation of an AGS layered onto chrysotile tailings collected from the Clinton Creek asbestos mine. Acidgenerating substances included ground pyrite, sulfidic tailings from the abandoned Kam Kotia mine site in northern Ontario, Canada and laboratory grade sulfur.

Experimental Section

Site Description and Sampling. The Clinton Creek asbestos mine is located 77 km northwest of Dawson City, Yukon, Canada. Photographs of the open pit and tailings pile are shown in Supporting Information (SI) Figure S1. The bedrock composition includes ultramafic rocks consisting of serpentinite, harzburgite, lherzolite, dunite, and pyroxenite, most of which have been completely serpentinized. The serpentine minerals are predominantly chrysotile and antigorite (*12*). Prior to closure in 1978, the mine produced an average waste to ore ratio of 5.5:1 and accumulated approximately 10 Mt

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of tailings (*12*). These tailings consist primarily of fibrous chrysotile and massive serpentinite with minor amounts of magnetite, calcite, dolomite, magnesite, quartz, clinochlore, and pyroaurite (*2*). Weathering of these tailings since emplacement has resulted in the formation of magnesium carbonate crusts that contain hydromagnesite, dypingite, and nesquehonite (*2*).

Grab samples of serpentinite with veins of fibrous chrysotile were collected from the Porcupine open pit. Chrysotile tailings, with minimal visible carbonate crusts, were collected from a depth of 0.5 m and stored in plastic bags. During three years of fieldwork, water samples were collected from the open pit pond and Wolverine Creek that flows along the base of the tailings pile. Puddles that were found in topographic lows at the base of the pile were sampled in two separate years. Details regarding sample collection and analysis are provided in the SI.

Column Leaching Experiments, Phase 1. The aim of this one-month long experiment was to contrast biotic versus abiotic oxidation of an AGS and the effects on chrysotile dissolution. Columns consisted of either ground pyrite or elemental sulfur layered onto chrysotile materials from the Clinton Creek mine. These materials included (1) chrysotile tailings, (2) ground serpentinite, and (3) acid-washed chrysotile tailings, which were all sorted with an 8 mesh (<2.36 mm) sieve. The serpentinite hand specimen, collected from the open pit (SI Figure S1), acted as fresh tailings containing minor amounts of bedrock carbonate, but lacking secondary carbonate minerals. The acid-washed tailings were prepared using 1.0 N acetic acid in order to have carbonate-free systems (method described in the SI).

The columns were assembled in 10 mL sterile syringes and contained 10 g of chrysotile material packed on top of 1 cm³ of glass wool (SI Figure S2). Net-acid generating (NAG) tests (described in the SI) were performed on mixtures of ground pyrite and chrysotile tailings to determine the maximum amount of AGS that could be used (based on complete oxidation of the pyrite) without producing acidic leachates. A mixture containing 4% ground pyrite (final pH 7.94) was found to be suitable and equivalent amounts of sulfur, in terms of acid-generating potential, were used (eqs 3 and 4).

$$\text{FeS}_2 + 15/4\text{O}_2 + 7/2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 4\text{H}^+ + 2\text{SO}_4^{2-}$$
(3)

$$2S^{0} + 3O_{2} + 2H_{2}O \rightarrow 4H^{+} + 2SO_{4}^{2-}$$
(4)

The pyrite columns contained 0.417 g (4.0% by total weight), 0.870 g (8.0%) and 1.36 g (12%) of ground pyrite that was layered onto the chrysotile material. The elemental sulfur columns contained 0.218 g (2.1%), 0.447 g (4.3%), and 0.685 g (6.4%). In addition to these six columns, corresponding abiotic columns as well as duplicate control columns with neither pyrite nor sulfur were assembled.

Plastic caps were placed on top of each column to limit evaporation and 1.7 mL microcentrifuge tubes were used to collect leachates. The biotic-pyrite columns were inoculated with 250 μ L of an *A. ferrooxidans* culture (1.3 × 10⁶ cells/ml) per day over a five-day period. Sulfur, colonized with *A. thiooxidans* (7.0 × 10⁸ cells/g), was used in the biotic-sulfur columns. These microorganisms are able to oxidize ferrous iron and reduced sulfur compounds, versus reduced sulfur compounds, respectively, and produce sulfuric acid as a byproduct of metabolism (*13*). For leaching and to support growth of the *Acidithiobacillus* spp., each column received 2.0 mL (5 × 400 μ L) of a basal salt solution (pH 5.6, equilibrated with atmospheric CO₂) containing (per L dH₂O): 0.03 g (NH₄)₂SO₄, 0.01 g K₂HPO₄, 0.025 g CaCl₂· 2H₂O each week for one month. It should be noted that *Acidithiobacillus* spp. are chemoautotrophic and therefore use CO_2 from the atmosphere rather than organic carbon for growth. The SI provides details on the chemical and bacteriological methods used in this experiment.

Phase 2. The goals of this experiment were to determine leaching trends for the chrysotile tailings over one year and to demonstrate the treatment of sulfidic tailings from an acid mine drainage site while using them to enhance chrysotile dissolution. Columns contained either sulfidic tailings from the Kam Kotia mine (details in the SI) or elemental sulfur layered onto chrysotile tailings. NAG tests, performed on mixtures of sulfidic and chrysotile tailings, indicated that a mixture of 25% sulfidic tailings by weight would not generate acidic leachates (final pH 7.48).

Six columns (10 mL sterile syringes; SI Figure S2) contained 10 g each of chrysotile tailings (<2.36 mm) and either used sulfidic tailings (20, 25, and 30 wt. %) or elemental sulfur (6.5, 8.5, and 12.5 wt. %) for an AGS. The sulfidic tailings and sulfur contained viable populations of *A. ferrooxidans* (7.9 × 10^7 cells/g) and *A. thiooxidans* (4.9 × 10^8 cells/g), respectively. Duplicate control columns that lacked any AGS were also assembled. Over one year, these columns received a weekly 1.0 mL pulse of basal salt solution. A replicate 25% sulfidic tailings column was sampled after two months to examine secondary mineral precipitates using scanning electron microscopy (SEM) and to provide a pH profile of the column. The SI provides details regarding SEM and the chemical and bacteriological methods.

Results and Discussion

Clinton Creek Water Chemistry. The Clinton Creek site provides water chemistry data for a system that lacks an intrinsic sulfidic bioleaching component. The Mg-rich waters on site are a result of the weathering of ultramafic bedrock and tailings via atmospheric deposition of carbonic acid. Complete water chemistry for all samples collected is shown in SI Table S1. The Porcupine open pit pond had an average pH of 8.4 and total alkalinity of 217 mg HCO₃⁻/L. Cation abundances were Mg (avg. = 409 mg/L) \gg Ca (avg. = 109mg/L) \gg Na > K > Si and SO₄²⁻ (avg. = 1900 mg/L) was the major anion. This relatively closed system results in substantial evaporation as indicated by the high chlorine concentration (avg. = 33 mg/L). Oxidation of sulfides, observed on some pit walls, is the likely source of dissolved sulfate. Pyrite oxidation (eq 3) generates acid that would likely react with serpentinite thereby releasing Mg and Si into the water. The Wolverine Creek forms a small pond between the two lobes of the tailings pile (SI Figure S1) and had an average pH of 8.9 and alkalinity of 238 mg HCO_3^-/L . The major cations for the pond were $Mg > Ca \gg Na > Si > K$. The high pH is a result of the close contact with the tailings pile and the lower Mg and Ca concentrations of the pond water in comparison to upstream source water suggest precipitation of carbonate minerals. In regards to carbonate minerals, the two ponds are only supersaturated in respect to aragonite, calcite, dolomite, and magnesite.

Puddles, found at the base of the tailings, are remnants of earlier rain events. It should be noted that the spring melt or a heavy rain event would result in leaching of the tailings pile into Wolverine Creek and the loss of dissolved magnesium and the potential for greater CO_2 sequestration at this site. Magnesium (avg. = 165 mg/L) was the dominant cation with HCO_3^- (avg. alkalinity = 347 mg HCO_3^-/L) and SO_4^{2-} (avg. = 413 mg/L) being the two major anions. The puddle water was supersaturated in respect to magnesite, hydromagnesite, and although undersaturated in respect to nesquehonite, it would likely become supersaturated upon further evaporation. Sulfate concentrations are comparable to those of Wolverine Creek upstream of the tailings pile and can be attributed to oxidation of sulfides in the country rock.



FIGURE 1. The one-month long leaching trials of phase 1 showed enhanced dissolution of the chrysotile tailings with the addition of either ground pyrite or elemental sulfur colonized with *Acidithiobacillus* spp. compared to the abiotic controls.

The puddles had a very high Mg:Ca ratio (>100:1) and the high alkalinity and low dissolved silicon suggest dissolution of magnesium carbonates as rainwater percolated through the tailings. This is perhaps a result of magnesium carbonate minerals coating silicate minerals. In general, these mine waters provide a baseline for comparison of the Mg concentrations obtained from leaching experiments conducted in this study.

Column Leaching Experiments, Phase 1. The addition of either ground pyrite or elemental sulfur, comparing abiotic versus biotic, were used to enhance weathering of the chrysotile tailings, ground serpentinite, and acid-washed tailings. The chrysotile tailings contained 36.7 wt. % magnesia (XRF data in SI Table S2). Figure 1 displays the Mg concentration versus time for the columns containing chrysotile tailings and SI Figures S3 and S4 are of graphs displaying the data from the columns containing ground serpentinite and acid-washed tailings, respectively.

The amount of Mg released from the columns was proportional to the amount of AGS added to the column. Magnesium concentrations were greatest in columns containing chrysotile tailings, followed by ground serpentinite and acid-washed tailings. This is the result of there being both bedrock and secondary carbonate in the tailings whereas the ground serpentinite only contained primary carbonate and the acid-washed tailings contained neither. In total, the biotic-pyrite columns released 52 mg (0.26% of the total Mg present in the columns) of magnesium in comparison to 35 mg (0.18%) released from the abiotic-pyrite columns. SI Table S3 lists the amounts of Mg released from all the leaching trials conducted in this study. The biotic- and abiotic-sulfur columns released totals of 100 mg (0.50%) and 9.8 mg (0.05%)of magnesium, respectively. For comparison, the control columns containing only chrysotile tailings, ground serpentinite, and acid-washed tailings released 1.1 mg (0.05%), 0.2 mg (0.01%), and 0.03 mg (0.00%) of Mg, respectively. The

leachates from all of these columns had pH values >8.5, which demonstrates the neutralization capacity of the chrysotile materials.

The columns mimic a vadose zone and provide an ideal environment for growth of *Acidithiobacillus* spp. At the end of the experiment, the biotic-pyrite columns supported viable populations of *A. ferrooxidans* (avg. = 1.5×10^7 cells/g). The 12% biotic-pyrite column containing ground serpentinite had the highest population of *A. ferrooxidans* (3.3×10^7 cells/g) and produced the highest Mg concentration (2050 mg/L) of the pyrite columns. The biotic-sulfur columns contained viable populations of *A. thiooxidans* (avg. = 1.6×10^8 cells/g) and 3400 mg/L was the highest Mg concentration.

In order to place the experimental data into a broader context, they are compared to predictions from the far from equilibrium, pH-dependent chrysotile dissolution rate law established by Thom and Dipple (14) that defines the flux of magnesium (FMg in mol/m²/s) by eq 5.

$$LogFMg = -0.22pH - 10.2$$
 (5)

Only columns that incorporated acid-washed chrysotile tailings (surface area of 10.47 m²/g based on BET measurement and 6:4 ratio by mass of fibrous to massive chrysotile) are considered because magnesium carbonate minerals have been removed. In comparing the magnesium concentrations in the leachates from the abiotic-sulfur columns to the control columns, there was no abiotic enhancement of chrysotile dissolution, which is consistent with observations that noncolonized elemental sulfur is hydrophobic and relatively nonreactive. Therefore, only the biotic-pyrite (avg. total mass of Mg = 4.1 mg), abiotic-pyrite (2.6 mg), and biotic-sulfur (8.1 mg) columns that showed significant chrysotile dissolution over four weeks were modeled (SI Table S4); average pH values of solutions in contact with the AGS measured at the top of the columns were 3.9, 5.0, and 2.6, respectively. Based on the pH profile of a column with an AGS (SI Figure S5), there is a distinct reaction zone (mm scale) immediately



FIGURE 2. In the one-year long leaching trials (Phase 2), magnesium concentrations were greatly increased with the use of either sulfidic mine tailings or elemental sulfur used as an acid-generating substance. The graphs are labeled with the weight percentages of the sulfidic tailings and elemental sulfur added to the columns.

below the AGS, similar to the zone of eluviation in a soil profile, where the vast majority of chrysotile dissolution likely occurs. The pH of the solution in contact with the AGS as measured at the top of the columns is taken as the pH of this reaction zone. The column material always remained moist and the frequent addition of solution over four weeks would perturb the approach to chemical equilibrium in this reaction zone. The modeled results for average total magnesium leached from the biotic-pyrite, abiotic-pyrite, and bioticsulfur column sets were 4.3, 2.5, and 8.3 mg of magnesium, which are in good agreement with our experimental results. The acceleration in magnesium release caused by layering an AGS onto chrysotile tailings is consistent with the experimentally determined pH dependence of chrysotile dissolution. Although acid generation caused by oxidation of the AGS is greatly accelerated by a biological catalyst, the increase in dissolution rate can be explained as a pH effect.

Phase 2. Sulfidic tailings and sulfur were used as the AGS for this year-long experiment. The Kam Kotia tailings contain pyrite, pyrrhotite, chlorite minerals, quartz, and minor amounts of Cu and Zn sulfides (XRF data in SI Table S5.

Figure 2 displays the Mg and S concentrations as well as pH values for the AGS and leachates versus time.

Columns using sulfidic tailings produced sharp increases in Mg concentrations during the first five weeks followed by a somewhat irregular signal and then a gradual decline in later weeks. Sulfur concentrations generally followed those of magnesium and attests to the positive correlation between acid-generation and the release of Mg. The initially high Mg concentrations are primarily attributed to the dissolution of bedrock and secondary carbonate in the tailings and partly because of greater acid-generation in earlier weeks. Acidgeneration would decline as sulfides became depleted, as seen by the declining sulfur concentrations and the increase in pH values of the sulfidic tailings (avg. pH, initial = 2.2, final = 2.4). The irregularities in Mg concentrations are symptomatic of the heterogeneity of the tailings and possibly conduit flow in the columns.

Columns containing 20, 25, and 30% sulfidic tailings released 132 mg (5.96%), 139 mg (6.28%), and 224 mg (10.1%) of magnesium over the year, respectively. During the course of the experiment, rusted horizons advanced down the

columns. The 30% column, predicted to produce acidic leachates based on the NAG test, had a rusted horizon that was 3.8 cm thick and advanced to 0.5 cm from the bottom of the column. Leachate pH values ranged from 9.0 near the beginning of the experiment to 8.3 in the final week, except for the 30% column that showed a steady decline to 7.1. This decline in pH and advancing "rusted" horizon suggests that acidic leachates would have been produced if the experiment were extended beyond one year.

Metal concentrations (Fe, Cu, Zn) in leachates were minimal in the columns using sulfidic tailings as an AGS. SI Figure S6 displays concentrations of Si and Fe \pm Cu \pm Zn versus time. The columns containing 20 and 25% sulfidic tailings did not show trends of increasing metal concentrations during the year, but had occasional pulses of relatively high metal concentrations, presumably because of conduit flow. For example, the 20% column had pulses of 103, 4.8, and 7.2 mg/L (Fe \pm Cu \pm Zn) on weeks 4, 26, and 42, respectively. Excluding these pulses, average metal concentrations (Fe \pm Cu \pm Zn) for the 20 and 25% columns were 0.28 and 0.14 mg/L, respectively, with Fe being the major metal (96%). However, leachates from the 30% column did have declining pH values that corresponded to increasing metal concentrations in later weeks.

Macroscopically, the replicate 25% sulfidic tailings column (SI Figure S5) exhibited distinct zones of eluviation and illuviation. The pH profile showed a significant pH shift in the rusted horizon (from pH 2.2 to 8), which caused metals to precipitate within the column. The rusted horizon contained a variety of secondary mineral precipitates that were predominantly iron hydroxides that were associated with chrysotile fibers (SI Figure S7). Minor amounts of Cu, Zn, and As were detected using energy dispersive spectrometry (EDS) in some of the precipitates. One concern is that these precipitates appear to coat and possibly render surfaces nonreactive, which would lead to a decrease in Mg silicate dissolution.

In the phase 2 columns utilizing sulfur, the 8.5 and 10.5% sulfur columns showed sharp increases in Mg concentrations during the first five weeks followed by a slight decline then a gradual increase in later weeks (Figure 2). The initial release of magnesium is intuitively from the dissolution of carbonate minerals present in the tailings. The sulfur in the columns likely experienced some neutralization at the sulfur/tailings contact. For example, the sulfur in the 6.5% column, being relatively thin, was completely neutralized. Any level of neutralization of the sulfur in the 8.5 and 10.5% columns was not recognized because the pH measurements were taken at the surface. As time progressed, A. thiooxidans populations would have recovered and acidified the sulfur present in the columns. In the 6.5% column the sulfur became acidic by week 34, which coincided with increases in sulfur and magnesium concentrations in the leachate solutions. In all three columns, the gradual increase in dissolved sulfur and magnesium past week ~20 can be attributed to the recovery of bacterial populations. Rusted horizons, ~ 1 cm from the sulfur/tailings contact, formed from dissolution of magnetite, a minor component of the chrysotile tailings, within the upper region of the column followed by hydrolysis and precipitation further down.

Columns containing 6.5, 8.5, and 10.5% sulfur released 55 mg (2.48%), 317 mg (14.3%), and 261 mg (11.8%) of magnesium. The overlying sulfur in the 8.5 and 10.5% columns became more acidic (avg. pH, initial = 2.2, final = 1.9) as the *A. thiooxidans* populations became well established. The initial pH of the sulfur in the 6.5% column was nearly equal to that of the leachates (~8.5) before declining to pH 5.0 during the middle of the experiment and finally to 2.2 near the end as the bacterial population recovered. For each column, leachate solutions remained alkaline, pH ~8.6.

The amount of magnesium leached during the year-long experiment from carbonate minerals was accounted for by determining the percent carbon in the tailings (method described in the SI). The tailings contained 0.728% carbon that was assumed to be in the form of magnesium carbonate minerals. Dissolution of all the carbonate (assumed to be hydromagnesite) in 10 g of tailings would release 184 mg of magnesium. Even when assuming complete carbonate dissolution, both sets of columns must have promoted chrysotile dissolution to produce the leachates measured in these reactions systems. However, this is a dynamic system and not all of the carbonate in the columns would have been dissolved. Similar to a soil profile, the columns have zones of acid generation, eluviation, illuviation, and unreacted material (SI Figure S5). The zone of eluviation would have first been dominated by the reaction of sulfuric acid with carbonate minerals. As leaching progressed and a sufficient amount of chrysotile was exposed, neutralization would shift to silicate dissolution. Silicon concentrations (SI Figure S6) were typically less than 1.0 mg/L. However, the 30% sulfidic tailings and 8.5 and 10.5% sulfur columns had increasing concentrations of dissolved silicon in later weeks. Acidic conditions near the top of the column release silicon that is then precipitated as silica further down the column as the leachate solution becomes more alkaline. The shift from mainly carbonate dissolution to silicate dissolution can also be seen by examining the molar ratios of magnesium to sulfur in the leachate solutions. In both sets of columns, there is initially (weeks 1 and 2) only minor amounts of sulfuric acid being produced and dissolution of Mg carbonate minerals is mainly from reaction with the basal salt solution added to the columns. This is reflected in a high Mg:S molar ratio of the leachate solutions (avg. = 13:1). From weeks 3 to 18, the Mg:S molar ratio was on average 7:5, similar to the ratio that results from the reaction of sulfuric acid with hydromagnesite (5:3; eq 6).

$$Mg_5(CO_3)_4(OH)_2 H_2O + 3H_2SO_4 \rightarrow$$

 $5Mg^{2+} + 4HCO_3^- + 6H_2O + 3SO_4^{2-}$ (6)

The reaction of sulfuric acid with chrysotile (Mg:S = 1:1; eq 7) predominates during weeks 22-52, which is seen as a decline in the Mg:S molar ratio to an average 5:4.

$$Mg_{3}Si_{2}O_{5}(OH)_{4} + 3H_{2}SO_{4} \rightarrow 3Mg^{2+} + 2SiO_{2} + 5H_{2}O + 3SO_{4}^{2-}$$
(7)

The two control columns leached an average of 13.7 mg (0.62%) of Mg over the year, which would mostly have come from carbonate minerals. Data from these experiments suggests that the biooxidation of sulfur is a preferred method of leaching compared to the use of sulfidic tailings, which produced metal oxides that coated tailings material and could potentially reduce magnesium silicate dissolution. However, blending and layering of acid-generating tailings with acid-consuming tailings also has the potential to mitigate or prevent the onset of acid mine drainage (*15*). The addition and bioleaching of elemental sulfur has also been proposed as a means of processing low-grade nickel ore (*16*), and this study suggests it would be an effective leaching agent for ultramafic tailings.

Implications for CO₂ Sequestration in Mine Tailings. The use of acid-generating substances in conjunction with *Acidithiobacillus* spp. greatly enhanced the weathering of the chrysotile tailings. Magnesium concentrations in leachates were at least 1 order of magnitude greater than those obtained from control columns as well as waters analyzed from the Clinton Creek site. Implementing this bioleaching process on a larger scale could possibly produce leachates with even greater Mg concentrations. The phase 2 column containing



FIGURE 3. A schematic representation of a geoengineered tailings facility for CO_2 sequestration.

8.5% sulfur leached the most magnesium of all columns used in this year-long trial, 317 mg of magnesium in total or 14.3% of the magnesium in the column. Based on this scenario, 316 kt of magnesium would be leached from the 10 Mt of tailings during the first year. If downstream processing were able to precipitate all of this magnesium as hydromagnesite, then 125 kt of carbon (458 kt CO₂) would be sequestered (eq 8).

$$5Mg^{2+} + 4CO_3^{2-} + 2OH^- + 4H_2O \rightarrow Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$$
 (8)

One key challenge for the bioleaching process described in this study is that the carbonate in the tailings is dissolved during the leaching process. This is a drawback when using this process for the purpose of CO₂ sequestration. However, the magnesium released into solution is still available to form carbonate minerals "downstream", which was observed in the leaching experiments with magnesium carbonate being precipitated from some leachates. The Clinton Creek tailings have been emplaced since 1978 and have accumulated significant amounts of secondary carbonate (2, 9, 12). Therefore, these tailings may not be suitable for bioleaching because the secondary carbonate minerals that coat the silicate minerals in the tailings would preferentially react with the acid thereby decreasing the initial silicate dissolution rates, i.e., there could be a net loss of carbon prior to any gains. In contrast, fresh tailings (e.g., ground serpentinite used in this study) from active mines that have minimal or no amount of carbonate would be most suitable as a feedstock for bioleaching. In this situation, the use of an intensive sulfur-leaching process followed by downstream precipitation of carbonate minerals would be advantageous.

Ultramafic rock bodies are mined for valuable minerals and metals such as diamonds, nickel, asbestos, talc, and chromium (10). Similar to the Clinton Creek mine, tailings are usually piled and left barren, which are not optimal conditions for CO₂ sequestration. Figure 3 is a schematic of a tailings facility geoengineered for the purpose of CO₂ sequestration via mineral carbonation. Ideally, the tailings would be widely dispersed to maximize the capture of water (precipitation) and dissolved inorganic carbon. Control of water flow could be achieved by placing the tailings along a slight decline and by using an impermeable barrier to prevent water loss. As demonstrated in this study, the use of an AGS that is seeded with Acidithiobacillus spp. would greatly enhance the weathering of the tailings and produce leachates concentrated in magnesium. The amount of AGS would depend on availability, cost, neutralization potential of the ultramafic tailings, and the desired Mg concentration. Leachate waters would be directed into a closed basin where carbonate precipitation could be promoted by both evaporation and microbes, such as cyanobacteria (17, 18). Bioleaching as described in this study represents a low cost, passive process that uses waste products for both acid generation and neutralization while accelerating mineral dissolution, which is the rate-limiting step for mineral carbonation. Implementing the measures described in this study could aid in optimizing CO_2 sequestration and may enable ultramafic mine tailings to be used as viable carbon sinks.

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Supporting Information Available

Details for the Kam Kotia site, bacteriological and chemical methods, and additional figures for this study are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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