Review

Strategizing Carbon-Neutral Mines: A Case for Pilot Projects

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Abstract: Ultramafic and mafic mine tailings are a valuable feedstock for carbon mineralization that should be used to offset carbon emissions generated by the mining industry. Although passive carbonation is occurring at the abandoned Clinton Creek asbestos mine, and the active Diavik diamond and Mount Keith nickel mines, there remains untapped potential for sequestering CO_2 within these mine wastes. There is the potential to accelerate carbonation to create economically viable, large-scale CO_2 fixation technologies that can operate at near-surface temperature and atmospheric pressure. We review several relevant acceleration strategies including: bioleaching of magnesium silicates; increasing the supply of CO_2 via heterotrophic oxidation of waste organics; and biologically induced carbonate precipitation, as well as enhancing passive carbonation through tailings management practices and use of CO_2 point sources. Scenarios for pilot scale projects are proposed with the aim of moving towards carbon-neutral mines. A financial incentive is necessary to encourage the development of these strategies. We recommend the use of a dynamic real options pricing approach, instead of traditional discounted cash-flow approaches, because it reflects the inherent value in managerial

flexibility to adapt and capitalize on favorable future opportunities in the highly volatile carbon market.

Keywords: carbon sequestration; carbon mineralization; mineral carbonation; bioleaching; biomineralization; mine tailings; magnesium carbonate; greenhouse gas emissions; carbon market; real options valuation

1. Introduction

Mines that generate ultramafic and mafic mine wastes (e.g., tailings) have the capacity to more than offset their greenhouse gas (GHG) emissions by sequestering carbon dioxide (CO_2) via carbon mineralization to create an environmental benefit while utilizing a waste product. Carbon mineralization, also known as mineral carbonation, involves the reaction of CO_2 with alkaline earth metal bearing silicate and hydroxide minerals to form carbonate minerals, thereby storing CO_2 in a stable form. Rapid conversion of naturally occurring ultramafic and mafic minerals at high temperature and high pressure using industrial reactors is technologically feasible (e.g., [1,2]); however, the costs of mineral pre-treatment and the energy economics of accelerating carbonation reactions from geological to industrial timescales remain serious obstacles [3].

Economic viability is critical for the adoption and eventual commercialization of new processes within the mining sector as it must be cost-effective from a user perspective and must provide an acceptable return for investors. Because of the energy intensity required for mining and processing natural bedrock and carbonation in industrial reactors, the International Energy Agency has ruled out the likelihood of adopting carbon mineralization processes; traditional valuation methodologies estimate their cost for fixing one tonne of CO_2 to be between $50 and $100 U.S. [4], far exceeding current world carbon prices, which range from the European Union Emissions Trading System (EU ETS; floating) price of approximately $6 U.S. to the UK carbon price floor (fixed) price of approximately $28 U.S. In addition to economic incentives, reducing GHG emissions will likely contribute to ensuring mining companies maintain their "social license to operate" [5].

To overcome economic impediments, considerable research has focused on developing and accelerating carbonation processes using alkaline rocks and waste materials under low temperature and pressure conditions [6–10]. Specifically, numerous studies have explored the use of ultramafic mine wastes as a potentially valuable feedstock for carbon mineralization [11–29]. Ultramafic and mafic mines generate vast quantities of mine tailings that offer a readily available, fine-grained feedstock for carbonation. As an indication of their reactivity, passive carbonation of ultramafic tailings has been documented at several sites under normal mining conditions [11,17,18,20,21,24,26,30]. Tailings storage facilities (TSFs) for ultramafic and mafic mine wastes are typically designed solely to hold tailings and recycle process water. In contrast, sulfidic mine tailings require a more sophisticated TSF design to prevent the generation of acid mine drainage [31]. Carbonation of ultramafic mine wastes could be accelerated by implementing strategies that enhance mineral dissolution, increase CO_2 supply, and facilitate carbonate precipitation at near-surface conditions using TSF design strategies that promote carbonation.

We review some of the proposed biotic and abiotic acceleration strategies including: bioleaching of Mg-silicates; increasing the supply of CO_2 via heterotrophic oxidation of waste organics, altering tailings management practices, and use of point sources with elevated CO_2 partial pressures (pCO_2); and biologically induced carbonate precipitation. Although these strategies have proven effective in laboratory-scale studies (e.g., [13,15,19,28,32,33]), pilot projects are crucially needed to evaluate strategies for accelerating carbon mineralization, which if successful and cost effective could be incorporated into TSF design with the purpose of sequestering CO_2. Discussion of these strategies is followed by the proposal of two scenarios for pilot projects, which if implemented at the mine-scale could render some mining operations carbon-neutral. We provide estimates of the operational costs of the proposed scenarios on a dollar per tonne of CO_2 basis and recommend the use of a real options valuation model (comparable to what one might use to price a biotechnology start-up) to better assess the potential of carbon mineralization strategies.

2. Mine Sites: Untapped Potential to Sequester CO_2

The mining industry is a major GHG emitter (e.g., [34]), and certain mines have the untapped capacity to significantly or completely offset their GHG emissions. Ultramafic and mafic mines generate massive quantities of tailings that are rich in Mg-silicate and hydroxide minerals such as the serpentine polymorphs chrysotile, lizardite and antigorite [$Mg_3Si_2O_5(OH)_4$], olivine group minerals such as forsterite [Mg_2SiO_4], and highly reactive oxides and hydroxide phases, e.g., brucite [$Mg(OH)_2$]. These tailings, which are otherwise a waste product, are a potentially valuable mineral feedstock for carbon mineralization because of their quantity, mineralogical composition, and high reactive surface areas that are generated during ore processing. Although felsic tailings may also act as mineral feedstock for carbonation reactions, ultramafic and mafic mine wastes have been the focus of most studies as these wastes are more reactive (e.g., [18,25]).
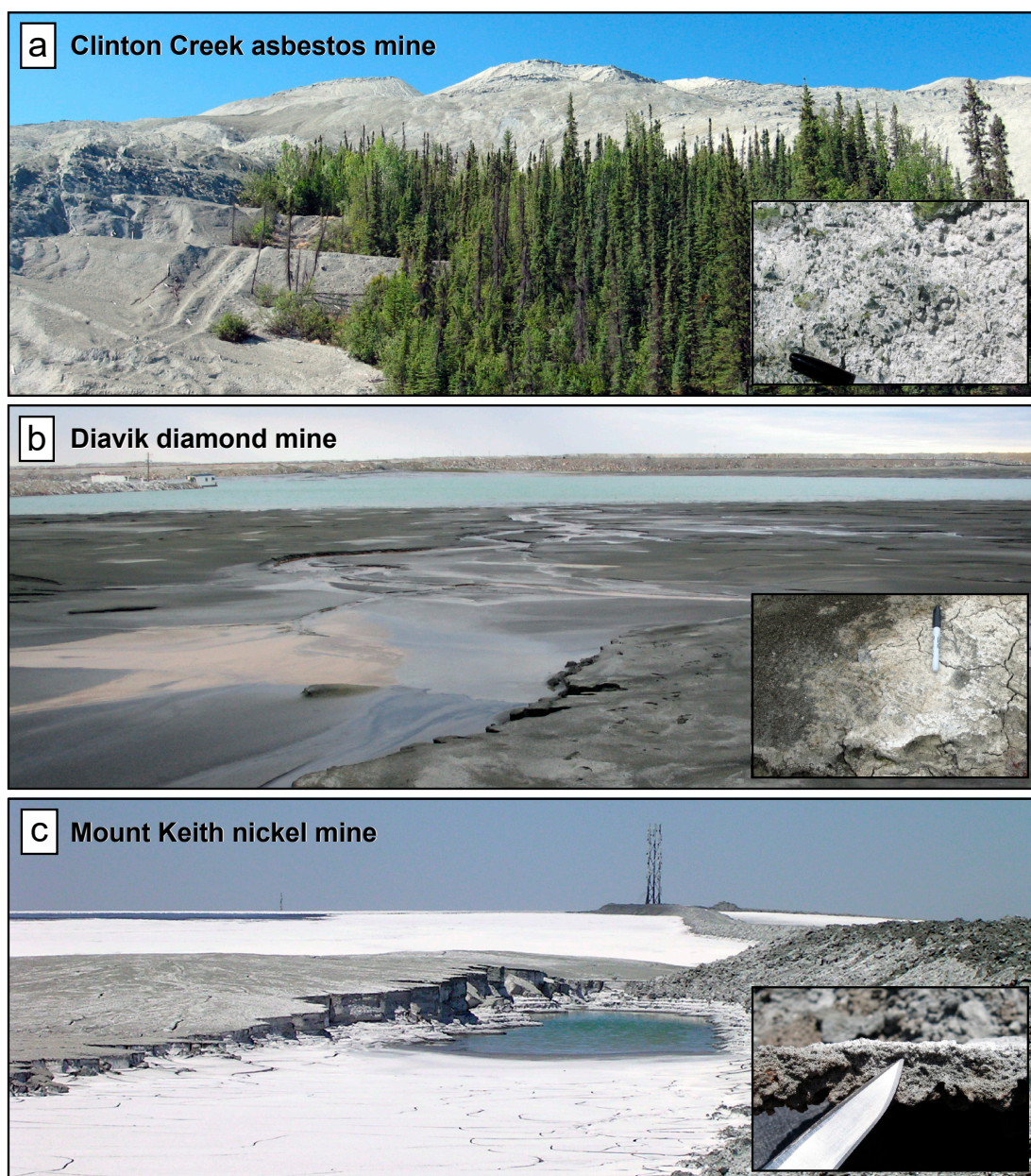
Global production of nickel, platinum group metals, asbestos, diamond, chromite, and talc generates ~419 Mt of ultramafic and mafic mine tailings annually [35]. Assuming complete carbonation, this provides the potential to sequester ~175 Mt CO_2/year [35]. On the scale of individual mining operations, certain mines have the capacity to more than offset their own GHG emissions, thereby providing a sink for other emissions sources. For example, complete carbonation of the ~11 Mt of tailings generated annually at the Mount Keith nickel mine in Western Australia [36] would sequester ~4 Mt CO_2/year as magnesium carbonate minerals such as hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$]. This represents a capture capacity of approximately 10 times the annual emissions generated by the mine. Although passive carbonation of mine tailings have been documented at mine sites under normal mining conditions, such as those at the Mount Keith nickel mine, the bulk of their capacity to sequester CO_2 remains untapped.

2.1. Comparative Studies of Ultramafic Mines

Our research investigating carbon mineralization at mine sites has focused largely on three sites: the abandoned Clinton Creek asbestos mine, and the active Diavik diamond and Mount Keith nickel mines (Figure 1). These mines have formed the basis of field, laboratory, and geochemical modeling studies aimed at developing the capacity to better utilize mine wastes as carbon sinks [11,13,15–21,28,37–40].

It is from this research that much of our understanding of carbon mineralization at mine sites and acceleration strategies are drawn. Each of these sites is characterized by distinct climatic and hydrological conditions and different tailings management practices, all of which have an impact on the rate and extent of carbon mineralization. Because the tailings from all three sites are mineralogically similar, it is possible to identify factors that enhance as well as limit weathering and carbonation of Mg-rich gangue minerals (Table 1).

Figure 1. Tailings storage facilities (TSF) for ultramafic tailings. (**a**) Abandoned Clinton Creek asbestos mine in Yukon, Canada. Inset shows vertical efflorescent crust cementing chrysotile tailings (marker for scale). (**b**) Active Diavik diamond mine in Northwest Territories, Canada. Inset shows an efflorescent crust on surface of tailings (marker for scale). (**c**) Active Mount Keith nickel mine in Western Australia. Inset shows a surface efflorescent crust held up to show cross-sectional view (knife for scale). These carbonate crusts have formed from passive carbonation under normal mining conditions.

Table 1. Mine sites investigated for carbon mineralization.

Mine Site	Clinton Creek	Diavik	Mount Keith
Location	Yukon, Canada	Northwest Territories, Canada	Western Australia
Commodity	asbestos (abandoned)	diamonds (active)	nickel (active)
Environmental data [13,36,41]			
Climate	subarctic	subarctic	desert
Mine site GHG emissions (kt CO_2e/year)	n/a	219	382
Onsite power generation (CO_2 point source)	n/a	yes	yes
Water usage (ML)	n/a	376 directed to TSF 72 treated sewage to TSF 12,491 discharged to Lac de Gras	9,534 in total 1,651 high quality 186 treated sewage effluent
Tailings production	~11 Mt in total	~2 Mt/year	~11 Mt/year
Process water [Mg + Ca] (mg/L)	~160 (pore water)	~40	~3,500
Mineralogical data [15,20]			
Major minerals	chrysotile (~88 wt %)	lizardite (48 wt %), forsterite (25 wt %)	antigorite/lizardite (~81 wt %)
Minor minerals	dolomite, magnesite, quartz, magnetite, pyroaurite	vermiculite, phlogopite, calcite, muscovite, plagioclase, quartz, diopside, almandine-pyrope	iowaite, magnesite, woodallite, magnetite, chromite, dolomite, chrysotile
Highly reactive phases for carbon mineralization	trace brucite	n/a	brucite (~2.5 wt %)
MgO (%)	~37%	~33%	~40%
Secondary Mg-carbonates from passive carbonation	nesquehonite, dypingite, hydromagnesite, lansfordite	nesquehonite	hydromagnesite
Carbon mineralization [11,17–19]			
Passive carbonation rate (g CO_2/m^2/year)	~6,200	374–418	2,400
GHG emission offset from passive carbonation	~82 kt CO_2 total (1978 to 2004)	~0.2% of total GHG emissions	~11% of total GHG emissions
Potential GHG emissions offset based on full carbonation (kt CO_2) to hydromagnesite	~3,700 kt CO_2 in total from chrysotile	~670 kt/year from lizardite; ~230 kt/year from forsterite	3,400 kt/year from antigorite/lizardite; 166 kt/year from brucite

Clinton Creek is located in the subarctic, ~80 km northwest of Dawson City, Yukon, Canada. The mine produced approximately 11 Mt of chrysotile dominated tailings (Table 1) during its operational lifetime from 1967 to 1978 [21]. The tailings pile was initially situated on a hilltop overlooking a creek, but has since slumped downslope to cover the hillside (Figure 1a).

Of the two active mines studied, the Diavik diamond mine, another subarctic site, is located approximately 300 km northeast of Yellowknife, Northwest Territories, Canada. Most of the residual kimberlite waste (2 Mt/year; dominantly lizardite and forsterite) is piped as slurry into a natural basin used as a TSF [17]. The tailings are partially submerged in a pond in the center of the basin (Figure 1b). The Mount Keith nickel mine is located in the desert of Western Australia, ~630 km

northeast of Perth. It produces ~11 Mt of tailings per year that are transported as a suspension in hypersaline process water ([Mg + Ca] ≈ 3500 mg/L) and deposited from nine risers in a TSF that is ~16.6 km^2 in area (Figure 1c). The TSF has a slight slope from the natural topography, allowing process water to be collected and recycled. Antigorite and lizardite comprise the majority of the tailings and brucite, a highly reactive phase, is present at minor abundance (Table 1).

The Diavik mine emitted ~219 kt of CO_2 equivalent (CO_2e) of greenhouse gases in 2011 and the Mount Keith mine emitted ~382 kt of CO_2e in 2004 [36,41]. Diavik has installed four wind turbines that are expected to reduce GHG emissions by 6%, suggesting that there is motivation to reduce GHG emissions [41]. Pertinent information regarding these three sites is summarized in Table 1.

2.2. Passive Carbonation at Mines: Rates and Limitations

CO_2 sequestration at mines results from weathering and carbonation of ultramafic and mafic tailings that are exposed to Earth's surface conditions. We refer to this process as passive carbonation because it occurs without human mediation and is not an intended outcome of the TSF design. Passive carbonation has been documented at Clinton Creek [18,20], Diavik [17,21], and Mount Keith [11,19] as well as other abandoned and active mine sites in Canada, United States, Australia, and Norway [24,26,30,42].

Mineral dissolution rates are significantly increased due to the high reactive surface area of tailings in comparison to natural bedrock, which provides Mg in solution that is available for carbonation (e.g., [11]). For example, the Mg concentration of water draining from Clinton Creek chrysotile tailings is ~160 mg/L in comparison to the natural background Mg concentration in local creek water of ~70 mg/L [13]. Evapoconcentration and uptake of atmospheric CO_2 into tailings pore waters can result in the precipitation of hydrated Mg-carbonate minerals (Equation (1); e.g., hydromagnesite), which are common low-temperature weathering products of natural serpentine minerals and brucite (e.g., [43,44]).

$$5Mg^{2+} + 4CO_3^{2-} + 2OH^- + 4H_2O \xrightarrow{\text{Evap.}} Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O \tag{1}$$

Although these phases are metastable compared to magnesite [$MgCO_3$], precipitation of hydrated Mg-carbonate minerals occurs more readily due to kinetic limitations on magnesite precipitation at near-surface temperatures (e.g., <60 °C) [45,46]. Thus, metastable phases including lansfordite [$MgCO_3 \cdot 5H_2O$], nesquehonite [$MgCO_3 \cdot 3H_2O$], dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$], and hydromagnesite typically form from weathering of ultramafic mine tailings [11,18,20,21,26]. Mg-carbonate minerals commonly form at tailings surfaces as efflorescent crusts (insets in Figure 1), thick hardpans, and at depth within tailings as cement between mineral grains [18].

The rate of passive carbonation depends on the characteristics of the tailings (e.g., mineralogy and grain size), climatic conditions (e.g., temperature and precipitation), process and pore water chemistry, and the design of the TSF. The tailings at the abandoned Clinton Creek mine have sequestered an average of 6200 g CO_2/m^2/year within hydrated Mg-carbonate minerals since the mine closed in 1978 (Table 1) [18,47]. This rate is based on analyses of the upper ~1 m of tailings where exposure to atmospheric CO_2 would be greatest. In contrast, natural uptake of atmospheric CO_2 during silicate weathering in river catchments in the Russian and Canadian arctic and subarctic is estimated to be 4.4–10.3 g CO_2/m^2/year [48,49]. The elevated weathering rates observed at Clinton Creek are a consequence of the subaerial exposure of the fine-grained tailings and spreading of the pile due to

slumping. Although the climatic conditions are similar at Diavik, passive carbonation at this site only sequesters an estimated 374–418 g CO_2/m^2/year [21]. Here, reaction rates are limited by the TSF design, which has the majority of tailings submerged in a pond. Passive carbonation rates of 2400 g CO_2/m^2/year are estimated at Mount Keith in an operational central discharge TSF [19], which offsets annual mine emissions by ~11% [19]. Rates are likely faster at Mount Keith than at Diavik because of its warm, dry climate (*i.e.*, high evaporation rates), saline water chemistry (*i.e.*, greater cation concentrations), and a TSF design that allows for subaerial exposure of tailings enabling greater ingress of atmospheric CO_2 and evapoconcentration of pore waters. These rates of passive carbonation are achieved under non-ideal chemical conditions (e.g., CO_2 limited), leaving the majority of tailings un-carbonated. Thus, further carbonation requires acceleration strategies.

2.3. Evidence for Microbial Activity at Mine Sites

TSFs are neither designed for carbon mineralization nor as habitats for microbial communities that could facilitate carbon mineralization. However, the possibility of rendering certain mines carbon-neutral, has led to investigation of microbial processes for mediating carbon mineralization within TSFs. Ultramafic and mafic mine tailings typically lack abundant energy sources and/or limiting nutrients for microbes that might otherwise contribute to mineral dissolution and/or precipitation. For instance, microbial counts of heterotrophic bacteria in the Clinton Creek and Mount Keith tailings have modest populations of 10^1 to 10^5 colony forming units (cfu)/g as determined by the standard plate count method. In contrast, soils and sediments possessing high microbial activity, typically possess on the order of 10,000 different species of bacteria with total populations of up to 10^{10} bacteria/g [50]. At the aforementioned mines, there are examples of microbe-carbonate interactions and microbially mediated processes that could potentially be harnessed to sequester CO_2 (Figure 2).

A striking example of microbially mediated carbonate precipitation are the carbonate microbialites found in an open pit pond at Clinton Creek (Figure 2a–c) [37]. These microbialites are columnar (up to 15 cm tall; Figure 2b) and presumably began forming in the flooded open pit after the mine closed in 1978. Precipitation of aragonite entombs calcifying microbes such as cyanobacteria, which may be observed using scanning electron microscopy (SEM) of acid-etched thin sections (Figure 2c) [37]. At Diavik and Mount Keith, field observations suggest that process waters in TSFs are oligotrophic and do not support extensive microbial growth. Still, biofilms and microbial mats, dominated by cyanobacteria, are found on pit walls at Diavik (Figure 2d–f) and within drainage channels at Mount Keith (Figure 2g–i), respectively. Exposing these biological samples to dilute acid while observing under a light microscope generated visible bubbles of CO_2 (Figure 2f,i), thereby determining the presence of submicron-scale grains of carbonate minerals amongst non-carbonate grains [51]. These examples of microbe-carbonate interactions suggest that a mining environment can foster microbial communities capable of mediating carbonate precipitation, which introduces a potential biological pathway for sequestering CO_2 at mine sites.

3. Strategies for Accelerating Carbon Mineralization

Carbon mineralization in mine wastes depends on the rates of mineral dissolution, supply of CO_2 into solution, and carbonate precipitation (driven by processes such as evaporation and alkalinity

generation). Thus, strategies to accelerate carbon mineralization must target one or more of these processes (Figure 3) [35]. Passive carbonation under normal mining conditions is limited by the supply of CO_2 [11,16]; however, conditions could arise in an acceleration scenario in which mineral dissolution or carbonate precipitation become rate limiting. Thus, strategies that enhance mineral dissolution/precipitation and CO_2 supply could be deployed within a TSF alone or in combination. Table 2 summarizes the key processes and considerations of some potential acceleration strategies.

Figure 2. Evidence of microbe-carbonate interactions at Clinton Creek (**a**–**c**), Diavik (**d**–**f**) and Mount Keith (**g**–**i**). (**a**) Open pit pond at the Clinton Creek asbestos mine with (**b**) carbonate microbialites along the pond periphery (marker for scale) (after [37]). (**c**) scanning electron microscopy (SEM) micrograph of acid-etched thin section revealing filamentous cyanobacteria previously entombed in aragonite. (**d**) Open pit wall at Diavik showing water drainage (arrow) and biofilms (**e**) on rock surfaces (width of photograph is ~30 cm). (**f**) Biofilm is dominated by cyanobacteria and upon reaction with dilute acid, bubbles of CO_2 become visible under light microscopy. (**g**) Drainage channel for the TSF at Mount Keith with (**h**) floating microbial mats (marker for scale). (**i**) Light micrograph of microbial mat with tailings grains and small bubbles of CO_2 produced from reaction with dilute acid indicating an association with carbonate minerals.
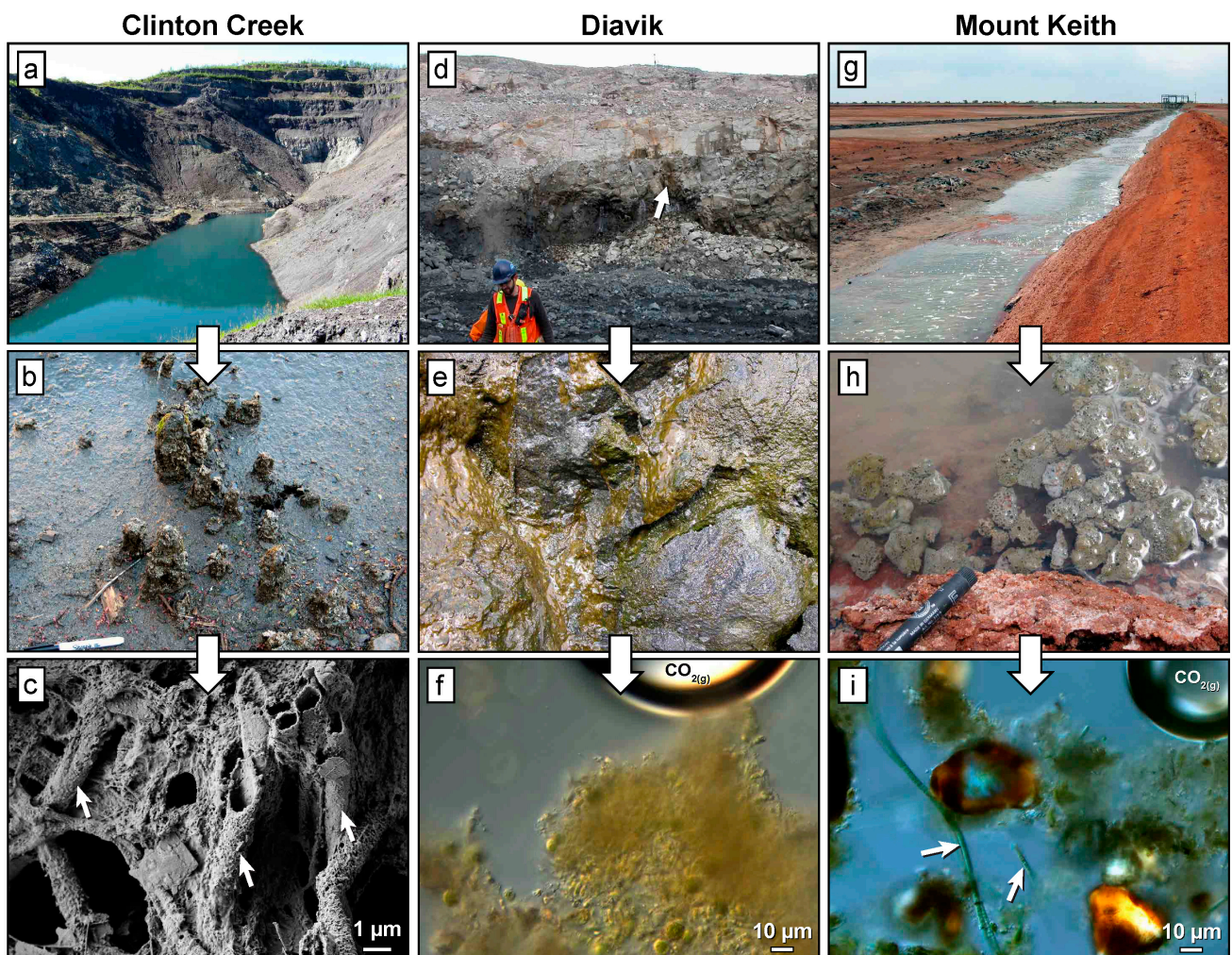
Table 2. Summary of accelerated carbon mineralization strategies.

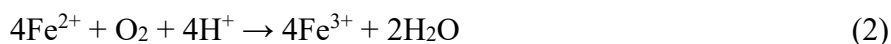| Strategy	Rate-limitation targeted	Processes	Example technology	Key considerations
Bioleaching	• Mineral dissolution	• Acid generation by oxidation of sulfides/sulfur by *Acidithiobacillus* spp.	• Heap leaching	• Availability of inexpensive acid-generating substances
Enhanced passive carbonation	• Mainly CO_2 supply, also mineral dissolution and carbonate precipitation	• CO_2 ingress from atmosphere into mine waters	• Air sparging or *in situ* aeration	• Available resources (e.g., land) • Tailings permeability • Abundance of highly reactive phases
CO_2 injection	• Mainly CO_2 supply, also mineral dissolution and carbonate precipitation	• Injection of CO_2-rich gas or fluids into tailings	• Carbon capture and storage into subsurface pore space	• Abundance of highly reactive phases • Point source of CO_2 available
Oxidation of waste organics	• Mainly CO_2 supply and mineral dissolution, also carbonate precipitation	• Heterotrophic oxidation of organics for *in situ* supply of CO_2	• Wastewater supply to TSF (e.g., Diavik and Mount Keith)	• Availability, degradability, and carbon content of waste organics
Bioreactors	• Carbonate precipitation • CO_2 supply if incorporating carbonic anhydrase	• Microbial carbonate precipitation (e.g., alkalinization) • Biomass production	• Wetlands for treating mine drainage • Bioreactors for biofuel production	• Available resources (e.g., water) • Rates of carbonate biomass production • Quality of biomass (e.g., lipid content)

Figure 3. A conceptual diagram consisting of the three fundamental processes that may be rate-limiting for carbon mineralization within a TSF. Strategies for accelerating carbon mineralization target one or more potential rate limitations (modified from [35]).
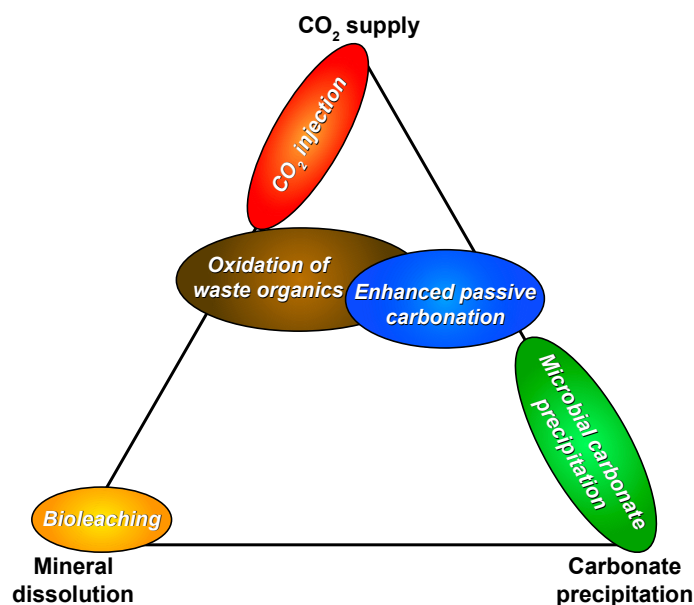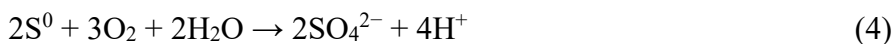

3.1. Bioleaching of Ultramafic Mine Tailings

The reactivity of ultramafic mine waste is enhanced by increased surface area due to mineral processing, yet dissolution rates remain sluggish at the alkaline pH of process waters [11,38,52–55]. Consequently, it may be advantageous to accelerate tailings mineral dissolution by altering the pH of process waters. The pH-dependent dissolution rates for some common ultramafic tailings minerals such lizardite [55], chrysotile [38], forsterite [53] and brucite [54] have been experimentally determined and generally increase with increasing acidity. Several studies have demonstrated enhanced dissolution of serpentine and olivine by microbes mainly through the production of organic acids (e.g., [56–58]).

Heap leaching has been used at some mining facilities to enhance metal extraction from low-grade sulfidic ores of copper, gold, uranium and zinc [59–61]. These sulfidic materials provide an ideal habitat for acid-generating microbes (e.g., *Acidithiobacillus* spp.) that greatly accelerate the generation of sulfuric acid for mineral dissolution and metal leaching [62–65]. A similar process using acid-generating bacteria could be applied to TSFs with ultramafic mine tailings. Appropriate bacteria for bioleaching include *Leptospirillum ferrooxidans* (an iron oxidizer), *Acidithiobacillus ferrooxidans* (an iron and sulfur oxidizer), and *A. thiooxidans* (a sulfur oxidizer) [64,66]. These bacteria are chemoautotrophs meaning they obtain their energy through chemical processes and use CO_2 as a carbon source, which is important for carbon sequestration. Sulfuric acid is generated through the biooxidation of sulfur-bearing minerals, containing reduced iron (Equations (2) and (3) using pyrite as an example) and elemental sulfur (Equation (4)). At low pH values, ferric iron catalyses pyrite oxidation resulting in considerable acid generation (Equation (3)).

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \tag{2}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{3}$$

$$2S^0 + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+ \tag{4}$$

Under acidic conditions (pH < 4), acidophilic bacteria can generate acid at a rate of up to 10^5 times faster than abiotic processes [67,68].

With regard to ultramafics, bioleaching has been applied to low-grade ultramafic nickel ores containing sulfide minerals for metal recovery [69–75]. Zhen *et al.* [74] used a consortium of *L. ferrooxidans*, *A. ferrooxidans*, and *A. thiooxidans* to bioleach nickel-bearing sulfide ore from the Jinchuan mine, China. The ore contained a host of Mg-bearing minerals, dominantly olivine and antigorite as well as minor abundances of sulfide minerals, including pyrrhotite [FeS] and pentlandite [(Fe,Ni)$_9$S$_8$]. Through serial culturing, the microbial consortium was able to tolerate Mg concentrations of up to 25 g/L. Qin *et al.* [73] used this consortium for bioleaching a 500-tonne heap that was irrigated by a network of pipes and drippers. Purge solution chemistry during pre-leaching had Mg concentrations of 45.0–55.0 g/L and during bioleaching of 24.0–26.0 g/L. This is 10 to 10^3 times the concentration of Mg that is available to form carbonate minerals in TSF process water at Clinton Creek, Diavik and Mount Keith (Table 1).

In the case of ultramafic tailings in many TSFs, including those at Clinton Creek, Diavik and Mount Keith, there may be insufficient energy sources (e.g., sulfide minerals) to support acid-generating microbes. A potential strategy for cultivating these microbes in TSFs involves amending tailings with an acid-generating substance, such as waste sulfides or elemental sulfur [13]. Using Clinton Creek chrysotile tailings, either waste sulfides or elemental sulfur were layered onto tailings (Figure 4a) in column experiments to support viable populations of *A. ferrooxidans* (avg. = 1.5×10^7 cells/g) and *A. thiooxidans* (avg. = 1.6×10^8 cells/g), respectively. Greater microbial populations and quantities of acid-generating substances resulted in greater leachate Mg concentrations. In comparison to controls lacking microbes, leachate waters from biotic columns with ground pyrite had Mg concentrations that were up to 26% greater, and in columns using elemental sulfur Mg concentrations were up to 580% greater (Figure 5b) [13]. There was good agreement between the experimental results and those predicted using a pH-dependent chrysotile dissolution rate law [38], hence geochemical modeling could be used in a predictive capacity. In year-long trials (Figure 4c,d), 10% to 14% of the Mg contained within chrysotile was leached from the columns using acid-generating substances colonized by *Acidithiobacillus* spp. [13]. Acid-generating substances were typically at pH ~2, whereas leachate solutions were pH ~8.5, as reaction with chrysotile neutralized acidity. Mg concentrations in leachates generated by those columns containing metal sulfides generally declined over the year, likely owing to the passivation of chrysotile surfaces by iron hydroxides [13], whereas Mg concentrations generally increased in columns using elemental sulfur, possibly owing to increasing populations of *A. thiooxidans*. In short, an addition of an acid-generating substance colonized by *Acidithiobacillus* spp. could significantly enhance the release of Mg ions by nearly two orders of magnitude with minimal intervention once the process was initiated.

A key consideration with bioleaching is to prevent the drainage of acidic waters (Table 2). Acid-base accounting is used for predicating the potential onset of acid mine drainage [76]. These same procedures could be applied to a bioleaching scenario to ensure that the neutralization potential of tailings is not exceeded [13]. The quantity of acid-generating material can be adjusted to maximize mineral dissolution, yet prevent acidic drainage.

Figure 4. Bioleaching of ultramafic mine tailings (after Power *et al.* [13]). (**a**) Schematic of a bioleaching column using an acid-generating substance colonized by *Acidithiobacillus* spp. for accelerating dissolution of Clinton Creek chrysotile tailings. (**b**) Average Mg concentration of leachate from one-month column experiments with comparison to abiotic controls and a control lacking pyrite and sulfur. (**c,d**) Plots of Mg (triangles) and Si (diamonds) concentrations *versus* time from year-long trials. pH of the sulfidic tailings and elemental sulfur (dashed lines) and the leachate solutions (solid lines) are also plotted.
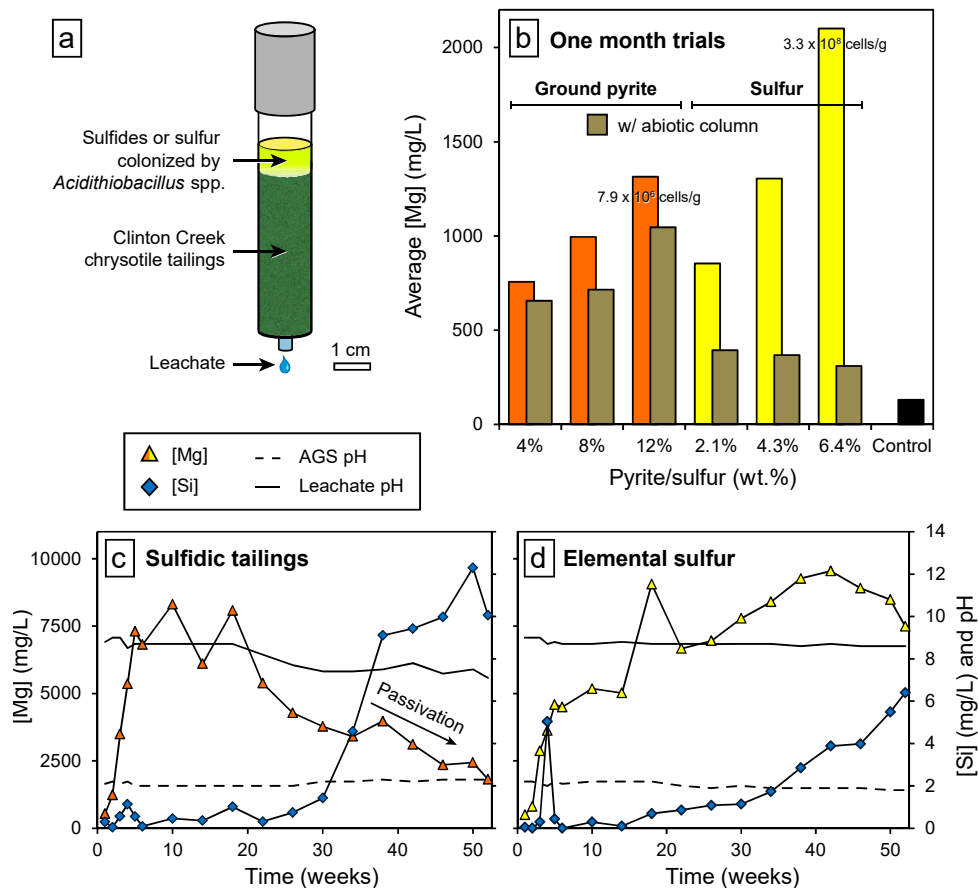
3.2. Increasing the Supply of CO$_2$

Stable carbon and oxygen isotopic compositions of hydrated Mg-carbonate minerals formed from weathering of ultramafic mine tailings at Diavik [17], Mount Keith [16], and other ultramafic-hosted mines in Norway [26] are consistent with carbon mineralization under CO$_2$ limited conditions. In addition, CO$_2$-depleted air has been documented to vent from chrysotile mining waste, further suggesting the CO$_2$ supply may be limiting for carbon mineralization [24]. This is likely due to the relatively slow gas to solution transfer and hydration of CO$_{2(aq)}$ [77], and the limited ingress of atmospheric CO$_2$ into tailings [19]. Here, we review both potential abiotic and biotic strategies for increasing the supply of CO$_2$ in a TSF.

3.2.1. Enhanced Passive Carbonation

Altering tailing deposition practices could significantly increase rates of passive carbonation by increasing the exposure of tailings to atmospheric CO$_2$ [19]. Upon deposition, tailings are at or near the

surface and thus are subject to weathering while they are exposed to meteoric or process water and atmospheric CO_2. As tailings are buried or immersed in TSF ponds, they receive less exposure to CO_2, which inhibits passive carbonation. Assima *et al.* [23] recommend an engineered design for efficient hydrodynamic conditions that would improve carbonation of chrysotile mining residues. Tailings management would aim to facilitate drainage and diffusion of CO_2. Wilson *et al.* [19] proposed that the rate of passive carbonation at Mount Keith could be enhanced by altering overall tailings deposition rates. Increasing the number of deposition points or increasing the areal footprint of the TSF would better control the thickness of tailings deposits and, hence, increase duration of exposure to atmospheric CO_2. Collectively we refer to these strategies as "enhanced passive carbonation" because the intended purpose of these human mediations is to enhance carbonation that occurs passively under normal mining conditions. Carbonation could be further enhanced by circulation of air throughout tailings piles to increase the exposure of reactive phases to CO_2 [19]. This is similar to existing technologies for *in situ* aeration (*i.e.*, air sparging), an established method for bioremediation of contaminated groundwater where increased O_2 concentrations stimulate growth of aerobic heterotrophs (e.g., [78,79]).

Some considerations for enhanced passive carbonation are the abundance of highly reactive phases (e.g., oxides and hydroxides) that react more readily with atmospheric CO_2, the availability of land to increase the areal footprint of a TSF, the permeability of tailings, the climate, and the economic viability of deploying the required infrastructure (Table 2).

3.2.2. CO_2 Injection

Injection of CO_2-rich gases or fluids directly into ultramafic tailings has been proposed for accelerating carbon mineralization [28]. This would significantly increase the supply of CO_2 that could then be mineralized by either abiotic or microbial means. Direct carbonation of mine tailings requires both mineral dissolution and carbonate precipitation to occur simultaneously. Mineral buffering under high $p CO_2$ conditions can be sufficient to maintain circumneutral pH at conditions that may also allow for carbonate precipitation [28]. The carbonation of brucite, a highly reactive tailings mineral, can be accelerated by up to ~240 times over passive rates by supplying gas streams with CO_2 contents similar to power plant flue gas (10%–20% CO_2) [28]. The supply of CO_2-rich gas streams not only accelerates brucite carbonation by providing more CO_2, but also by increasing the HCO_3^- concentration of solutions, which interacts with the brucite surface and promotes dissolution [80]. Dissolution rates of some silicate minerals such as lizardite may also be modestly increased in the presence of HCO_3^- (e.g., [55]). This strategy is dependent on the availability of a CO_2 point source, such as might be provided by an on-site power plant ([81] and references therein). Injection of CO_2 would likely shift the overall carbon mineralization rate from being CO_2 limited to Mg-limited [40]. Injection of CO_2 into the subsurface, such as in saline aquifers, is currently being practiced (e.g., [82,83]) and there are pilot projects (e.g., CarbFix) for injecting CO_2 into mafic rocks [84,85]. These technologies could be adapted for injection into ultramafic mine tailings. An important consideration for CO_2 injection strategies is the proximity of the CO_2 point source to the TSF, as transport of CO_2 is costly (Table 2). The effective permeability of tailings should also be considered, as high injection pressures may be required to maintain a CO_2 flux through low permeability media, leading to higher operating costs [19].

Additionally, *in situ* carbonation may also lead to passivation of reactive surface areas and changes in permeability [86].

3.2.3. Oxidation of Waste Organics

Numerous studies have documented biologically induced carbonate precipitation by heterotrophic bacteria, including sulfate reducers, which use organics as a carbon source [87–90]. Waste organics could act as a CO_2 source given that heterotrophic bacteria may completely oxidize organic compounds to produce CO_2, which if not mineralized, will likely be released to the atmosphere (Equation (5)).

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \tag{5}$$

Mine camp sewage at Diavik and Mount Keith are ultimately fed to their TSFs for disposal. At Diavik, aerobic oxidation of organic matter produces CO_2 that may become incorporated into secondary carbonate minerals [17]. Given the small volume of treated sewage directed to the TSF, this is a relatively minor source of carbon (Table 1). Additional waste organics would be required to significantly increase carbon mineralization. For example, Mitchell *et al.* [91] suggest that municipal wastewater (~20 g urea/L) could be injected into the subsurface where bacterial ureolysis would generate alkalinity thereby inducing Ca-carbonate precipitation and fixing CO_2. Lindsay *et al.* [92,93] proposed amending mine tailings with waste organics for preventing the release of toxic metals through enhancing *in situ* microbial sulfate reduction. Use of peat, spent brewing grain, and municipal biosolids generated alkalinities of ~1000–2000 mg $CaCO_3$/L with $\delta^{13}C$ values (<−20‰) indicating that dissolved inorganic carbon (DIC) was supplied by oxidation of organics [92,93]. Biosolids may also be used for stabilizing and revegetating mine tailings [94–96]. In addition, leaching of Mount Keith and Diavik tailings using acetic acid has been shown to produce Mg-acetate solutions that foster considerable precipitation of dypingite when inoculated with a consortium of cyanobacteria and heterotrophic bacteria [15]. Heterotrophic metabolism, nitrification, and anaerobic fermentation may generate organic acids that promote mineral dissolution, whereas alkalinity generating processes such as denitrification and methanogenesis may induce carbonate precipitation [32,97]. When considering the use of waste organics, the quantity of available carbon and the biodegradability of the waste should be considered (Table 2). An abundant, easily accessible and degradable waste with high carbon content is likely to maximize CO_2 supply.

3.3. Bioreactors for Carbon Mineralization

In nature, silicate dissolution is often biogeochemically coupled to the precipitation of carbonate minerals by microorganisms [98]. A wide range of microbial metabolisms may induce carbonate precipitation under suitable geochemical conditions [98–101]. Alteration of water chemistry through microbial metabolism may occur within the microenvironment surrounding a cell, within the interstitial water of a biofilm or microbial mat, or at a larger scale, such as a body of water. If a suitable habitat and favorable geochemical conditions were provided, microbial carbonate precipitation could operate in a TSF for the purpose of carbon sequestration. Relevant reviews of microbially induced carbonate precipitation are provided by Riding [102], Dupraz *et al.* [101], Jansson and Northen [103], and Kamennaya *et al.* [104].

Photosynthesis as a biological pathway for carbon mineralization is advantageous as CO_2 is used by microbes as a carbon source (e.g., [104]). Photoautotrophs possess carbon-concentrating mechanisms that enable them to increase the concentration of CO_2 inside their cells to as much as three orders of magnitude greater than in the extracellular environment [105,106]. DIC is transported into the cell and converted to HCO_3^- by the enzyme, carbonic anhydrase (CA). HCO_3^- anions enter the carboxysome via diffusion, at which point they are converted to CO_2 by CA and subsequently into biomass (Equation (6)) [102]. This process generates OH^- ions and results in a pH increase (e.g., alkalinization) in the cell's microenvironment that can induce carbonate precipitation in geochemical environments that have sufficient cation and DIC concentrations [107] (Equation (6)).

$$HCO_3^- + H_2O + hv \rightarrow CH_2O + OH^- + O_2\uparrow \qquad (6)$$
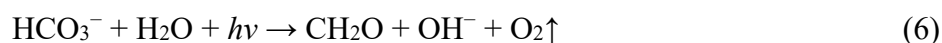
Photoautotrophs may also induce carbonate precipitation by the adsorption of cations onto their cell walls, thereby increasing cation concentrations in the microenvironment [108–110]. Cell walls often have a net-negative charge because of the presence of functional groups such as carboxyl groups. In addition, extracellular polymeric substances (EPS) produced by cells, typically contain "excess" negatively charged functional groups [101]. Cations adsorbed to functional groups may become partially dehydrated, allowing for carbonate ions (CO_3^{2-}) to react with the otherwise inaccessible cations (Equation (7)) [111–113].

$$R.COO^- + [Mg(H_2O)_6]^{2+} \rightarrow [Mg(H_2O)_5(R.COO)]^+ \qquad (7)$$
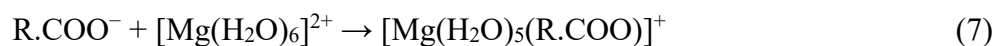
This is particularly important in the case of Mg^{2+} because it is usually bound in an octahedrally-coordinated inner hydration shell of six water molecules, and the exchange rate of water molecules in this shell is much slower than other cations such as Ca^{2+} [114–117]. An alternative precipitation mechanism involves intracellular precipitation of amorphous carbonates, as demonstrated by a recently discovered cyanobacterial species of the order *Gloeobacterales* [118]. This could offer another biological pathway for CO_2 sequestration as these cyanobacteria may exert greater control over carbonate precipitation.

Experimental studies by Power *et al.* [51] and Shirokova *et al.* [119] have demonstrated cyanobacterially-mediated precipitation of Mg-carbonate minerals from Mg-HCO_3 waters. In previously unreported results, the consortium used by Power *et al.* [51] was able to induce carbonate precipitation in experiments using water sourced from the open pit at Clinton Creek. After six weeks of incubation, pH had increased from 8.4 to 9.2 and Mg concentration had decreased from 356 to 278 mg/L, whereas the pH of the control remained constant and Mg concentration increased to 401 mg/L due to evapoconcentration. SEM imaging revealed that a fine-grained carbonate mineral had precipitated within the biofilm of filamentous cyanobacteria (Figure 5a). In another study, unicellular green algae (*cf. Dunaliella* sp.) induced carbonate precipitation from waters produced by leaching of Diavik and Mount Keith tailings using various acids [15]. Abundant carbonate precipitation occurred in systems that had used acetic acid for leaching, which provided an additional carbon source (Figure 5b,c). In contrast, Mg- and Ca-silicate minerals coated cell surfaces (Figure 5d) in systems that relied on atmospheric CO_2 as the sole source of carbon, indicating that CO_2 supply from the atmosphere was rate-limiting for carbon mineralization. Consequently, additional carbon sources or more proficient means of delivering atmospheric CO_2 into solution are required to accelerate microbial carbonate precipitation.

Figure 5. Representative scanning electron micrographs from carbonate precipitation experiments showing microbe-mineral interactions. (**a**) Fine-grained carbonate precipitates (arrows) formed in association with filamentous cyanobacteria in experiments using water from the open pit pond at Clinton Creek. (**b**) Algal cells (arrows) on the surface of Ca-carbonate aggregate and (**c**) filamentous cyanobacteria on a large (~10 μm wide) rosette of dypingite (bottom right). Solutions produced by leaching of Diavik (**b**) and Mount Keith (**c**) tailings using acetic acid, which acted as an additional carbon source. (**d**) Algal cell completely encrusted by fine-grained Mg-Ca-silicates from solutions produced by leaching of Mount Keith tailings [15].
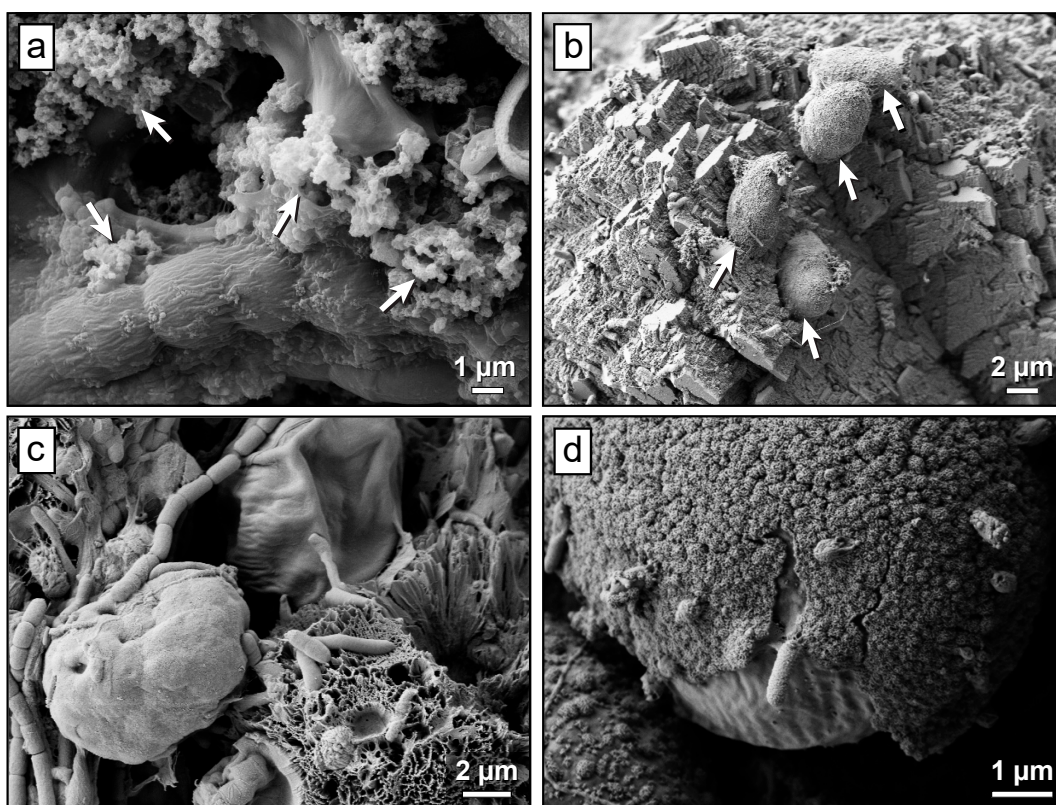
In the presence of elevated CO_2 concentrations, some species of cyanobacteria and microalgae experience an increase in growth rate, photosynthetic activity, and nitrogen fixation [120–125]. Greater microbial growth rates would result in an increased availability of the EPS-hosted reactive groups needed for cation concentration and dehydration. Increased levels of CO_2, which could be achieved within a TSF carbonation pond by bubbling concentrated CO_2 into the water, would stimulate biological activity while also providing increased availability of DIC for carbonate precipitation. For instance, in a raceway pond experiment *Chlorella* sp. and *Spirulina platensis* achieved 46% and 39% mean CO_2 fixation efficiency using an input CO_2 concentration of 10%, which is similar to the composition of flue gas [126]. An alternative means of increasing CO_2 supply involves the direct use of CA, which catalyzes the hydration of aqueous CO_2, for carbon mineralization. CA is produced by prokaryotes and eukaryotes and is actively being investigated as an additive for accelerating carbonate precipitation, typically as part of an industrial process [39,127–131]. A challenge associated with elevated CO_2 concentrations is that dissolving CO_2 into water decreases pH, and therefore decreases carbonate mineral saturation.

Photoautotrophic carbonate precipitation could be encouraged in bioreactors or open ponds "downstream" of a TSF such that the pond receives tailings process waters rich in cations [15]. Wetlands used for treating acid mine drainage [132,133] and bioreactors for biofuel production [134] are technologies that could be adapted for developing bioreactors for carbon mineralization. The global abundance of salt tolerant cyanobacteria make them a favorable target for growth in saline mine process waters. Organic-rich wastewater from mining camps would offer an inexpensive source of nutrients (e.g., nitrogen and phosphorous) for growth of phototrophs (Table 1). In addition to economic considerations, space and water required for cultivating microalgae and cyanobacteria must be considered (Table 2). There is potential to extend the industrial use of photoautotrophs by using the generated biomass for producing biofuels and other valuable by-products [134–136]. Few studies have investigated coupling of microbial carbonate formation with biomass production for the purpose of sequestering CO_2 [15,126,137].

4. A Case for Pilot Projects

Individual mines generate considerable amounts of GHGs from point sources, mainly from fossil fuel consumption for power generation, and distributed sources such as those from trucks and mining equipment. Protocols exist for mining operations to estimate their GHG emissions from fuel combustion and specific process-related activities (e.g., [138]). For instance, the Mount Keith nickel mine emitted ~382 kt of CO_2e in 2004 [36]. Comminution (~53%), flotation (~13%), and mining equipment (~34%) are key contributors to GHG emissions [139]. Point sources at mine sites offer a potential CO_2 supply for carbon mineralization, whereas, distributed sources can be offset either by direct capture from the atmosphere or by utilizing additional offsite CO_2 sources. At Mount Keith, the 11 Mt of tailings generated each year would sequester 3400 kt CO_2/year and 170 kt CO_2/year from complete carbonation of antigorite + lizardite and brucite, respectively to form hydromagnesite, which in total would offset mine emissions by approximately 10 times (Table 1). Prior to the construction of the centralized TSF at Mount Keith, field trials were conducted to develop better approaches to tailings storage. These trials consisted of six storage units (25 × 25 m) used to establish a range parameters including settling, consolidation and drying characteristics [140]. Pilot projects of a similar scale are crucially needed in order to assess the efficacy of strategies for accelerating carbon mineralization.

In this review, we have considered five strategies for accelerating carbon mineralization in TSFs: (1) bioleaching, (2) enhanced passive carbonation, (3) CO_2 injection into tailings, (4) oxidation of waste organics, and (5) bioreactors for carbon mineralization. Each of these strategies aims to minimize one or more of the potential rate limitations for carbon mineralization (Figure 3). These strategies may be modified or combined; for instance, combining the use of a bioreactor with elevated pCO_2 supplied by a point source. Naturally, there are advantages and disadvantages to each strategy, which may or may not be alleviated by the use of two or more complementary strategies.

A decision tree (Figure 6) is useful for outlining beneficial combinations of strategies that may be considered for pilot projects aimed at accelerating carbon mineralization within a TSF. Carbon mineralization strategies are best employed at mine sites that will generate Mg- and Ca-rich mine tailings. The overall design of a carbon mineralization pilot project within a TSF will depend on a number of site-specific factors. Key considerations include the availability of a point source of CO_2

(e.g., using CO_2 from flue gas) and the abundance of highly reactive phases. In addition, there are specific considerations for each strategy discussed in this review (Table 2). For example, an inexpensive source of an acid-generating substance (e.g., sulfidic tailings or waste sulfur) would need to be available for bioleaching. Climate has an overarching influence; a warm and wet climate will encourage microbial growth, whereas warm and dry climates will increase evapoconcentration of solutes. The local climate for some mine sites, such as Diavik in the Canadian subarctic, will present challenges to both abiotic and microbially mediated carbon mineralization. Here, we consider two of the numerous possible scenarios for the design of pilot projects based on the decision tree in Figure 6. The discussion of each scenario is based on knowledge and data gathered from the Mount Keith nickel mine (Table 1), the most thoroughly studied of the sites highlighted in this review.

Figure 6. Decision tree for developing a pilot project for accelerating carbon mineralization in mine tailings.

Decision tree for design of a pilot project
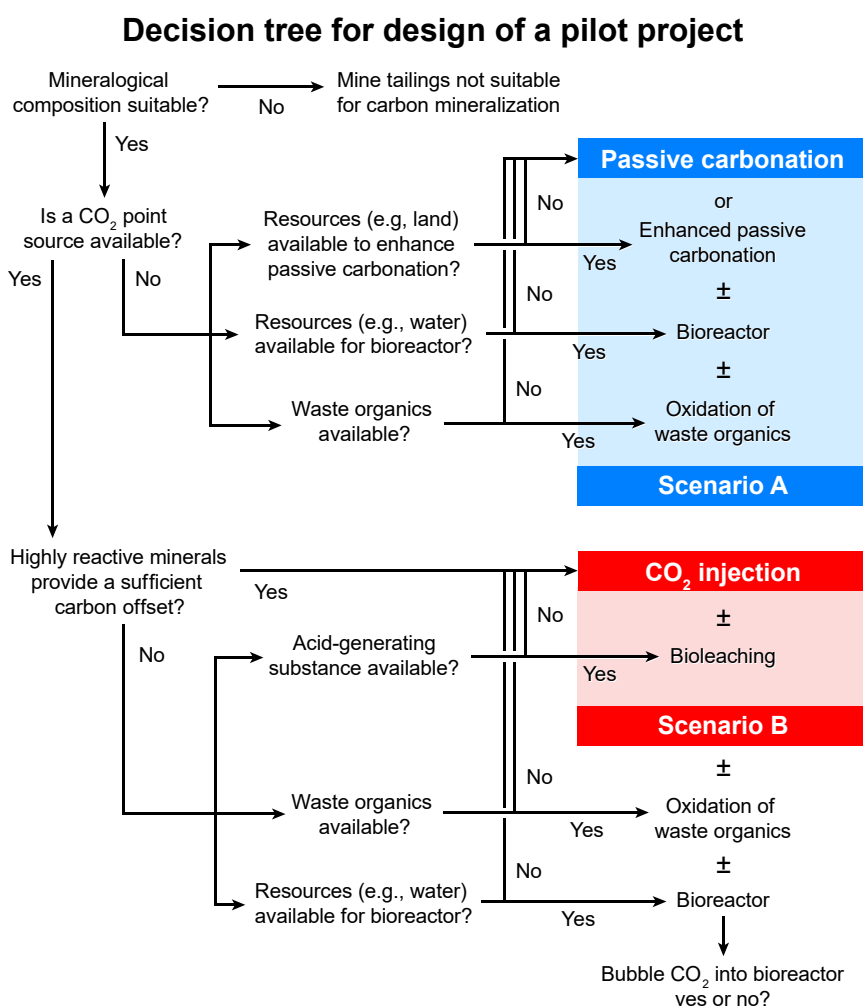
4.1. Scenario A

The pilot project described by Scenario A does not rely upon point sources of concentrated CO_2 (Figure 6). Carbon mineralization could be accelerated by enhanced passive carbonation, use of a bioreactor, and use waste organics as an additional CO_2 source. These three strategies are mutually compatible, *i.e.*, a TSF could be designed to use any combination of these three strategies.

Mount Keith has the greatest passive carbonation rates amongst the mines discussed in this review (Table 1). Factors facilitating carbonation at Mount Keith include the tailings mineralogy (81 wt % lizardite + antigorite and 2.5 wt % brucite), the large areal footprint (16.6 km^2) of the TSF, which, distributes tailings widely and allows for exposure to the atmosphere, a hot and dry climate with high evaporation rates, and the use of cation-rich bore water for tailings deposition [11,19,141]. The majority of hydromagnesite precipitation at Mount Keith results from reaction of brucite with dissolved atmospheric CO_2 near the surface of the TSF (<25 cm depth) [19]. Consequently, passive carbonation is in part controlled by the overall tailings deposition rate (~50 cm/year), where the duration of exposure to the atmosphere is significantly reduced by frequent deposition of fresh tailings [19,40]. Tailings deposition occurs from nine risers near the center of the TSF, which restricts most tailings deposition to a smaller, centralized area rather than ensuring even distribution over the entire area of the TSF. More even spatial distribution of tailings would result in longer atmospheric exposure times, allowing a greater extent of brucite reaction [19]. A pilot project could be used to determine the deposition rates for achieving optimal carbonation of brucite present in the tailings. Enhanced passive carbonation of an average brucite abundance of 2.5 wt % would sequester 166 kt CO_2/year or 44% of mine emissions in the form of hydromagnesite. The presence of hydrotalcite group minerals (5.8 wt % iowaite [$Mg_6Fe^{3+}_2(OH)_{16}Cl_2 \cdot 4H_2O$] and 2.9 wt % woodallite [$Mg_6Cr_2(OH)_{16}Cl_2 \cdot 4H_2O$]) may offer additional CO_2 storage capacity, although the extent to which these minerals could sequester CO_2 has not been fully assessed [12]. Additionally, it is not known to what extent Mg-silicate minerals are contributing dissolved Mg to carbon mineralization at Mount Keith; however, petrographic and mineralogical evidence from this and other mines indicates that serpentine and olivine minerals can be a major source of Mg. A pilot project could assess the contributions of hydrotalcite group minerals and Mg-silicates to carbon sequestration under field conditions.

A greenhouse-scale bioreactor has been used to demonstrate sequestration of carbon within biomass and Mg-carbonate minerals [33]. It is important to consider that the capacity for microbially mediated carbonate precipitation to sequester CO_2 is partially dependent on the volume of water available for a pond or bioreactor, whereas the rate is dependent on the microbial growth and carbonate precipitation rates that can be achieved in the presence of a given microbe, water chemistry, and climatic conditions. The Mount Keith TSF employs the natural topography of the site to collect tailings water for reuse in the ore processing circuit. A demonstration downstream bioreactor could be built at the current site of the water reclamation pond to promote simultaneous biomass production and carbon mineralization using leachate waters from the TSF. Microbial carbonate precipitation could potentially sequester ~53 kt CO_2/year in the form of carbonate minerals with an additional ~11 kt CO_2/year stored as biomass [15], which, in total, would offset GHG emissions by 17%. The estimate for annual biomass production assumes a conservative growth rate of ~35 mg dry biomass/L water/day under non-ideal conditions and a lipid content of 11%. Photoautotrophs could, however, represent a much more significant sink for carbon given that the median rate of biomass production for microalgae is ~200 mg dry biomass/L water/day and ~24% lipid content (determined from a review by Mata *et al.* [134]). At these rates, GHG emissions at Mount Keith could be offset by approximately 30%.

In total, Mount Keith uses approximately 11 GL of saline water each year [36]. The mine camp produces ~186 ML of wastewater each year, which is treated and discharged into the TSF. Typical wastewater contains 100 s of mg/L of dissolved organic carbon [142], which is an insignificant carbon

source for offsetting GHG emissions. The nearest city is Kalgoorlie (population $\approx$ 30,000), which is approximately 500 km south. Thus, there is no known source of additional, readily available waste organics. Nevertheless, field trials could assess the potential for mineralizing carbon from waste organics to test the extent to which this carbon may become mineralized.

4.2. Scenario B

Scenario B is based on the use of a point source of CO_2 such as could be supplied from an on-site power plant burning fossil fuels (Figure 6). Bioleaching could be deployed in combination with CO_2 injection. The choice of CO_2 injection would likely be made based on the reactivity of mine tailings with elevated pCO_2. For instance, Harrison *et al.* [40] estimate that carbonation of approximately 3 wt % brucite would be sufficient to offset point source emissions at Mount Keith and that tailings with approximately 6.5 wt % brucite would be sufficient to render many ultramafic-hosted mines carbon-neutral. In the case of Mount Keith, which has an average brucite abundance of ~2.5 wt %, CO_2 injection rates would need to be balanced with tailings deposition rates to ensure complete carbonation of brucite and thus prevent CO_2 leakage. CO_2 injection would likely shift the rate limitation from CO_2 supply, as in the case of passive carbonation, to cation-supply limited as the dissolution rates of the abundant Mg-silicate minerals are sluggish in comparison to highly reactive phases like brucite [40]. However, Daval *et al.* demonstrated that the dissolution rate of lizardite is increased by 5 times at pH 5 in solutions equilibrated with CO_2 as compared to CO_2-free solutions at the same pH [55], suggesting that CO_2 injection into ultramafic mine tailings may also increase silicate dissolution rates, thereby increasing the cation supply.

Application of the bioleaching process to the ultramafic mine tailings at Mount Keith could accelerate CO_2 sequestration by increasing the cation (e.g., Mg^{2+}) supply for carbonation. Bioleaching columns amended with elemental sulfur have been shown to release up to 14% of the available Mg in the columns with leachate concentrations of up to ~9500 mg/L (Figure 4d) [13]. In addition, bioleaching of low-grade nickel ore has been estimated to produce Mg concentrations in excess of 25,000 mg/L [73,75]. Reaction of brucite is largely responsible for hydromagnesite precipitation at Mount Keith. As a comparison, complete dissolution of brucite (~2.5 wt % of 11 Mt tailings/year) would contribute a Mg concentration of approximately 15,000 mg/L when considering the volume of saline water used at Mount Keith (~7900 ML, determined from total water usage minus high quality water usage; Table 1). Bioleaching would best be employed when there are additional carbon sources for mineralization.

CO_2 from nearby offsite point sources (e.g., other industrial operations and power plants) could also be utilized at mine sites, thereby providing a greenhouse gas benefit for other industries. Capture of atmospheric CO_2 can be expected to occur in parallel with mineralization of injected CO_2 as a consequence of enhanced passive weathering and atmosphere-water exchange occurring within tailings. These sources could prove useful for offsetting distributed CO_2 emissions from a mine.

4.3. Monitoring and Verification

In addition to evaluating acceleration strategies, pilot projects would provide an opportunity for rigorous testing of monitoring and verification techniques that are needed to determine the quantity of carbon that has been sequestered and the sources of CO_2. Rates of passive carbonation at Clinton

Creek, Diavik, and Mount Keith have been determined previously [17–20]. Sampling involved collection of grab samples (e.g., 50 to 500 g) of tailings from the surface and at depth (e.g., augering), which are adequate for most analyses [17,19,20]. Wilson *et al.* [20,21] used X-ray diffraction (XRD) data with Rietveld refinement for quantitative measurement of mineral phases including the "secondary" carbonate minerals that provide a sink for atmospheric CO_2 in tailings. This same approach would be effective for assessing enhanced passive carbonation in Scenario A. A combination of stable carbon and oxygen isotopic data and radiocarbon dating of carbonate minerals were then used to verify carbon sources [17,19,21]. Sampling techniques are easily upscaled as there exists detailed guidelines for obtaining representative samples for assessing environmental impacts of mine wastes (e.g., [143]), which could be adapted for determining the extent of carbon mineralization at the mine scale. In the case of bioreactors, monitoring of water chemistry can be used as a proxy for carbonate precipitation with corroborating evidence such as XRD and electron microscopy [33]. Biomass would be analyzed for its biochemical composition such as the valuable lipid content [15].

In Scenario B, bioleaching would need to be monitored through analysis of pore water chemistry, such as pH and Mg concentration, in order to assess the rate and extent of tailings dissolution [13]. Monitoring of microbial processes, such as determining the populations of acidophiles may also be necessary. Pronost *et al.* [24] have demonstrated the effectiveness of a bulk monitoring strategy for passive CO_2 sequestration in mine tailings. Their approach combines the use of infrared imaging to monitor heat released by exothermic carbonation reactions with direct measurement of atmospheric CO_2 concentrations from air vents and seeps in TSFs. Similarly, a pilot project could be instrumented to monitor the real-time progress of carbon mineralization in a CO_2 injection scenario. As carbon sequestration technologies are implemented, there will be greater emphasis placed on development of protocols for accurately assigning carbon credits to industry.

5. Estimating Operational Costs

This review recommends a variety of strategies that may be used in combination to realize emissions offsets. The approach presented here offers tremendous flexibility in terms of the level of emissions offsets that may be achieved for a broad range of operational costs. In Figure 7, the operational costs of carbon mineralization using mine wastes are illustrated in a conceptual model modified from Hitch and Dipple [144]. There exist two broad end members, (1) passive carbonation that offers modest offsets (e.g., 11% of annual emissions at Mount Keith in the form of hydromagnesite) at no cost increase in mine operations and (2) carbonation using industrial reactors that may achieve upwards to complete conversion (typically ~80% to 100% conversion to magnesite) at a high operational cost (~$50–100/t CO_2; [144,145]) (Figure 7). Using EU carbon market and UK carbon floor pricing of approximately $6 U.S./t CO_2 and $28 U.S./t CO_2, respectively, as of 1 January 2014, passive carbonation at Mount Keith can be valued at approximately $250,000 U.S./year and $1,200,000 U.S./year, respectively. At Mount Keith, which produces 11 Mt of tailings annually, complete carbonation of serpentine and brucite to magnesite would offset mine emissions by ~1200%. The strategies discussed in this review fall between these two end members.

Scenario A coupled enhanced passive carbonation, a bioreactor, and use of waste organics (Figure 7). The costs of enhancing passive carbonation (e.g., 44% of Mount Keith emissions) mainly relate to

infrastructure costs such as increasing the number of deposition points or areal footprint of the TSF. Thus, significant offsets could be achieved through altering tailings management practices with little additional operational costs. Enhanced passive carbonation can be valued at approximately $1,000,000 U.S./year (European market) or $4,700,000 U.S./year (UK carbon floor). Biomass production could offset the operational costs associated with a bioreactor used for carbon mineralization. The estimated costs of biofuel production vary from below to greatly exceeding current oil prices (~$70 to $3,900/barrel of oil) [146]. In our cost analysis of Scenario A, we have made the conservative assumption that a bioreactor would only be operated at break even taking into account current crude oil prices (~$100/barrel) and the UK carbon floor price of $28 t/$CO_2$. However, if biofuel production costs are less than oil prices, then a *profit* can be made while more permanently sequestering CO_2 as carbonate. The combination of enhanced passive carbonation and use of a bioreactor could potentially offset approximately 74% of mine emissions (44% from enhanced passive carbonation and 30% from an efficient bioreactor). Enhanced passive carbonation is limited by the quantity of highly reactive brucite present in the tailings, whereas, a bioreactor would be limited by the volume of water along with microbial growth and carbonate precipitation rates.

Scenario B involved CO_2 injection and bioleaching. The total costs related to carbon capture and storage (CCS) via injection into subsurface pore space can be subdivided into costs associated with CO_2 capture ($25–115/t CO_2), transport ($1–8/t CO_2/250 km at 5–40 Mt CO_2/year), and storage ($0.5–8/t CO_2). These costs are provided in a report by the Intergovernmental Panel on Climate Change (IPCC) [145]. Some mines have on-site power generation, such as at Mount Keith that provides an easily accessible, inexpensive source of CO_2 thereby eliminating much of the transportation costs. Capture and storage costs would be significantly reduced given that tailings are susceptible to carbonation by gas streams of ~10%–20% CO_2 (e.g., flue gas with no purification) [28] and the very shallow depths required for CO_2 injection into tailings. Assuming an on-site CO_2 source without purification, we have estimated a cost of $1.5/t CO_2 based on the lower range of costs given in the CCS report by the IPCC [145]. Power generation accounts for approximately 66% of emissions at Mount Keith, which if sequestered would be valued at $1,100,000 U.S./year (European market) and $6,700,000 U.S./year (UK carbon floor) including the sequestration cost of $1.5/t CO_2. Stolaroff *et al.* [147] estimate an operating cost of $8/t CO_2 using heap leaching of CaO- and MgO-rich industrial wastes. Power *et al.* [13] demonstrated that greater than 14% of the Mg in experimental bioleaching columns could be leached, assuming that only a year's worth of tailings were leached and that the Mg was carbonated to form hydromagnesite, then 480 kt CO_2 or 124% of mine emissions could be offset. Because the amount of CO_2 generated at Mount Keith is finite, carbonation of the excess Mg released by bioleaching would require use of offsite sources of CO_2. Mines commonly operate in remote locations, therefore we have considered a conservative sequestration cost of $8.5 based on transportation and storage costs of $8 and $0.5/t CO_2, respectively, for a total cost of $16.5/t CO_2 [145]. Using the European and UK carbon prices, minus the $16.5/t CO_2 operational cost estimate, Scenario B would produce a negative valuation of (minus) $4,000,000 U.S./year, *versus* a positive valuation of $5,400,000 U.S./year, respectively emphasizing the importance of carbon prices in implementation of carbon sequestration technologies. In using point sources of CO_2, carbonation is likely to be limited by mineral dissolution, a rate-limitation that can be overcome using bioleaching.

Figure 7. Plot illustrating emissions offset (%) *versus* cost of CO_2 sequestration technology ($/t CO_2) for a mine site based on data for the Mount Keith nickel mine. Plotted are passive carbonation, Scenarios A and B, and industrial carbonation along with the EU floating and UK fixed carbon prices. Any new technology is only financially viable when its cost is below the applicable carbon price.
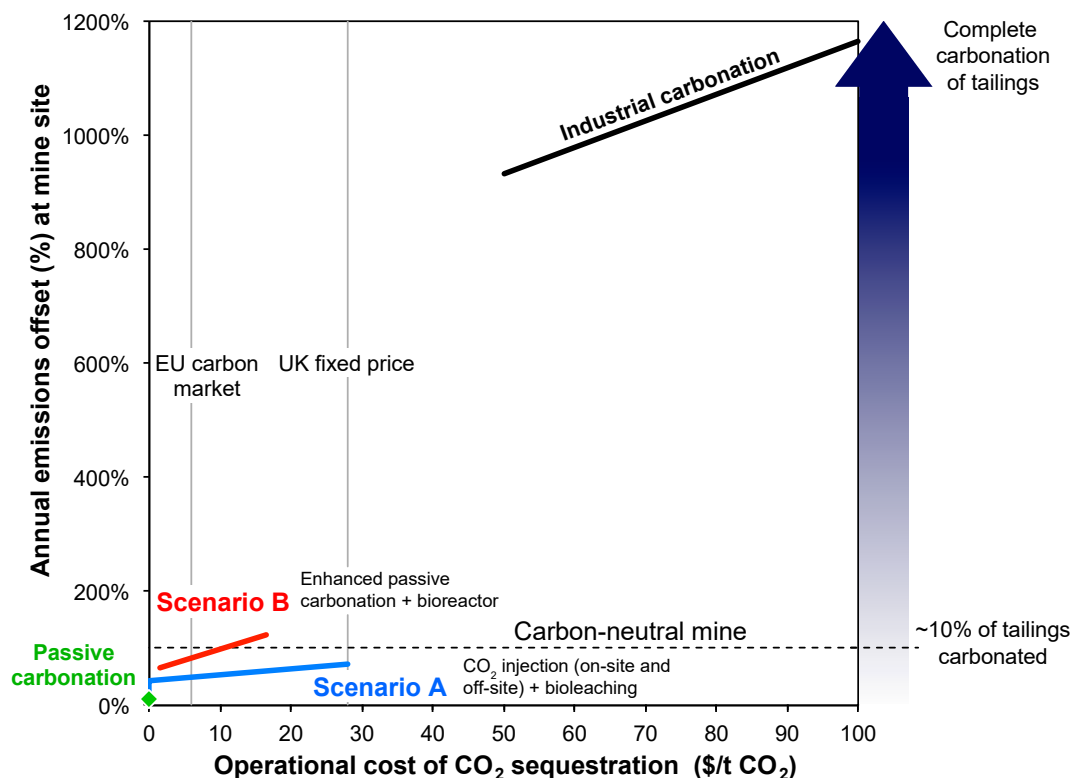
6. Carbon Price

It is evident that in order to assess the financial viability of the process, one must know both the amount of carbon sequestered and the carbon price. While there is no disagreement amongst economists that the true cost to society of burning one tonne of carbon is greater than its "private cost", there is no consensus about what that cost is [148]. This "social cost" of carbon (SCC) is the estimated price of the damage (unwanted climate change) caused by the increasing concentration of atmospheric GHGs; these costs are borne (at least, in part) by the world's taxpayers rather than the private cost to companies or individuals burning the GHGs. Different countries have their own policy responses to address carbon emissions: the two primary choices are a carbon market that places a 'cap' on carbon emission (but allows the market to determine the price) and a carbon tax that fixes the price of carbon (but allows the amount of carbon emissions to vary). Market-based, cap-and-trade systems are preferred and being used in India, Kazakhstan, New Zealand, Singapore, South Korea, the 31 countries covered by the EU ETS, as well as several sub-national systems in the U.S., Canada, China and Japan. The fate of existing carbon pricing policies in Australia is uncertain.

A market brings together buyers and sellers and price is determined by the forces of supply and demand; a price is simply what people are willing to pay. An issue with the market mechanism is that price is sometimes less than cost, which can lead to market failure. This is evident in the EU ETS; the per tonne EU ETS price peaked at $38 U.S. in 2006, dropped to $0.15 U.S. in 2007, and because of the

global financial crisis, prices have stayed low, providing no incentive for companies to lower CO_2 emissions or invest in carbon sequestration technologies. Recognition that carbon is grossly undervalued in the market came with the U.S. Interagency Working Group decision to raise its per tonne estimate of the SCC by 60% to $38 U.S. which may be considered a "rough and politically acceptable" price floor [148]. To combat the EU ETS market failure, the UK unilaterally added a carbon tax, a floor of approximately $28 U.S. to prop up the price of carbon. This created a "regulatory" arbitrage (*i.e.*, an opportunity to make a riskless profit by exploiting price differences in different markets) encouraging UK firms to relocate offshore to circumvent this unfavorable "tax", essentially shifting carbon emissions out of the UK and into continental Europe.

Arbitrage exists when market prices deviate from the true values; however, it also provides a mechanism to ensure that prices do not deviate substantially from true value for long periods of time. As with all markets, this carbon market arbitrage will soon disappear as governments close the obvious loopholes in realization that a worldwide carbon solution is required to correct mispricings. Mining companies must recognize that carbon-related tax penalties and incentives are proliferating around the world and the likelihood of "escaping such changes in a global economy are becoming more remote" [149]. There is also recognition that if carbon prices do not provide an incentive for companies to reduce emissions now, then companies will be forced to do more later, at a higher cost and with greater urgency [150]. It is certain that impending international collective action will establish a global carbon price (through tax, trading or regulation) that is more closely aligned with the SCC.

7. Valuation Model for Development of Carbon Mineralization in Mine Waste

The carbon mineralization strategies proposed in this review could overcome previous economic challenges to carbon mineralization by using existing ultramafic mine wastes as a feedstock for an industrial (bio)technological process that occurs at ambient temperature and atmospheric pressure over decadal timescales, *i.e.*, at rates that could become significant for GHG mitigation at mine sites. These innovations should significantly reduce the expected per tonne cost of carbon mineralization, but the widely-used net present value (NPV) approach to capital budgeting will still render these strategies economically unviable, until the market price for carbon price corrects. In making this decision, the mining company would only invest in a project if it has a positive NPV because this criterion is consistent with shareholder value maximization. Based on projections of how much future cash (S) a project will generate relative to its investment cost (X), NPV strives to calculate the value of a project today (S − X). NPV uses a discounted cashflow (DCF) valuation model, which is described as "discounted" because cash in the future is worth less than cash today (referred to as the "time value of money"). We discount the future cashflows at a cost of capital (r) that reflects the rate of return that the mining company would receive if it invested in a different project with similar risk. This DCF approach can be simplified by treating carbon mineralization of mine tailings as a valuation of a limited resource with a finite life [151–154]. This finite life resource approach collapses the traditional NPV to a multiplication of the quantity of carbon fixed times the carbon price (S) less the cost of carbon capture and sequestration (X). In Section 5, this simplified approach yielded the decision not to invest in Scenario B because S − X was negative.

A limitation with using NPV is that it implicitly assumes that the project is held passively and that the only decision that matters is the initial decision to invest. In reality, mine managers work within a dynamic operating environment and continuously make decisions over very long time periods such as expanding, contracting, abandoning, or simply waiting for more information before acting. Dixit and Pindyck [155] showed that the NPV decision-making criterion ignores the flexibility afforded by the embedded real (*i.e.*, non-financial) options because managers can obtain the right, but not the obligation to take a further strategic action at a future date. In a simplified financial options example, Minestock market price is $98, the call option "premium" is $4, "exercise price" is $100, and the "expiration date" is 1 January which means that today, the buyer would pay $4 (premium) to purchase the option, which would give would that person the right, but not the obligation, to purchase Minestock at the $100 exercise price on or before 1 January (expiration date). If Minestock price rises to $120, the buyer would be able to purchase Minestock for $100 and sell it at the market price of $120, making a net profit of $16 ($20 "profit" minus the $4 option premium). If the stock price only reached $99, the buyer would not exercise the option and it would simply expire. It is evident that the buyer was able to capture an unlimited upside potential in the increased stock price while limiting the downside loss to only the modest option premium. The mining company's investment in these carbon mineralization technologies should be valued using a real options approach because by making a modest investment in the development of carbon capture technologies (*i.e.*, the option premium) while the carbon price is low, a company will have the ability, but not the obligation to implement this technology quickly when the market carbon price corrects and benefit by capturing the unlimited upside potential.

Carbon mineralization has additional value because it provides managers with the flexibility to capitalize on favorable future opportunities or to limit losses by taking a future action. This value is driven by five attributes [156]. First is the value of the underlying asset (e.g., stock price, S), which in this case is the SCC. The second is the cost of sequestering carbon (e.g., exercise price, X). The third variable is the risk free rate (rf). The fourth is the variance (uncertainty or risk, σ^2) in the returns of the underlying asset, which in this case is the volatility of the price of carbon. The fifth is the time to get the project to maturity (e.g., expiration date, t). All things considered, the longer the time to maturity and the more volatility in the carbon price, the greater the value of the option.

A quick glance at Table 3, reveals that the real options valuation method has a much more complex decision making criteria compared to the simpler finite life resource and NPV models. A key difference between real options and the other two models is that real options consider the length of time until a manager must make the decision. The major shortfall of the two simpler models is their inability to incorporate operating flexibility and growth-opportunities faced by the company. The real options approach recognizes most projects are multi-stage and the decision to proceed, suspend, or abandon the project has value. First, since the mining company does not have to pay until it exercises the option, it can use that money for other investments today which takes into consideration the time value of money. Second, the mining company does not need to exercise the option and wait until the price of carbon is sufficiently high. NPV also does not consider the volatility of the carbon price, which is a key driver of the real options value. The greater the volatility of the carbon price, the more valuable the option will be for the mining company as it will be able to pursue this opportunity with its significant upside potential while the option completely insulates it from low carbon prices.

Table 3. Comparison of three valuation approaches.

Investment Opportunity	Finite Life Resource	Net Present Value	Real Options Valuation
Present value of the project's underlying assets	Price of carbon (S)	Price of carbon (S)	Price of Carbon (S_0)
Expenditure required to acquire the project assets	Cost to sequester carbon (X)	Cost to sequester carbon (X)	Cost of sequestering carbon (X)
Time value of money		Cost of capital (r)	Real risk free rate (rf)
Riskiness of the project assets		Incorporated into r	Volatility of carbon price (σ^2)
Length of time the decision may be deferred			Time to get project to maturity (t)
Decision Making Criteria: Invest if Value > 0	Value = S − X	$\text{Value} = \sum_{t=1}^{T} \dfrac{S-X}{(1-r)^t}$	Value is solution to the following partial differential equation: $$\max\left[\begin{array}{l}\dfrac{1}{2}\sigma^2 S_0^2 \dfrac{\delta^2 v}{\delta S_0^2} + (rf-k)S_0\dfrac{\delta v}{\delta S_0} - \dfrac{\delta v}{\delta Q} + \dfrac{\delta v}{\delta t}\\ +(S_0 - K_0) - \tau - (rf+\lambda_1)v\end{array}\right]=0$$ where: v(S,t) = mine value is a function of time and price Q = reserves k = commodity convenience yield λ = proportional rate of property tax τ = total tax

The real options approach recognizes the value can be realized in making an initial modest investment and then timing market entry [155]; this type of flexibility in corporate resource allocation has proven vital to long-term success in an uncertain and changing marketplace. One of the main implications of applying real options theory is that it helps companies battle, capitalize on and even befriend uncertainty [157]. Overlooking the options-like characteristic of this project could result in poor decision making and a missed opportunity. Real options have been around for more than three decades, yet are used by a very small proportion of managers because of "lack of expertise and knowledge" [158]. Companies who invest in this carbon mineralization technology in uncertain times will have future flexibility and can benefit from having the right, but not the obligation, to shift activities or take action in the future. The real options approach will capture the value inherent in the option for mining companies to enter into and profit from the highly volatile carbon market when the future price of carbon aligns with the SCC.

8. Challenges and Summary

Research teams will continue to advance our understanding of the fundamentals underlying carbon mineralization; however, overcoming the technological challenges of implementing carbon mineralization at mine sites requires investment from mining industry partners to test carbon mineralization processes at the pilot scale. Enhanced passive carbonation is a relatively simple approach with strategies being as straightforward as increasing the areal footprint of the TSF, yet more extensive carbon mineralization will require more involved engineering strategies. Many existing technologies such as bioreactors for biofuels could be adapted for the purpose of carbon mineralization at mine sites. There is universal recognition that carbon is currently undervalued in the market and this is problematic because there is no economic incentive for companies to reduce emissions. However, markets self-correct and we must recognize that the carbon market will become more efficient as market forces move the carbon price closer to its intrinsic value. In anticipation of this, companies should use a real options pricing approach, which will capture the inherent value associated with the flexibility for managers to defer, expand, contract, abandon, switch use, or otherwise alter a capital investment, in response to future carbon price volatility. Implementation of a combination of acceleration strategies as discussed in this review has the potential to render large mines carbon-neutral, should managers choose to invest in this option.

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Author Contributions

For this review, each author contributed to drafting and editing the manuscript. Ian M. Power coordinated the review and drafted the figures.

Conflicts of Interest

The authors declare no conflict of interest.

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