



POTENTIAL FOR IMPLEMENTATION OF MINERAL CARBONATION AS A CARBON SEQUESTRATION METHOD IN MINNESOTA

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POTENTIAL FOR IMPLEMENTATION OF MINERAL CARBONATION AS A CARBON SEQUESTRATION METHOD IN MINNESOTA: EXECUTIVE SUMMARY

Increasing concern about climate change has necessitated the assessment of ways to reduce greenhouse gas emissions such as carbon dioxide (CO₂), while concurrently increasing our preparedness for climate change and variability. For example, in 2007, the Minnesota Legislature set goals to reduce state emissions 15% by 2015, 30% by 2025, and 80% by 2050. These reductions can be achieved by reducing fossil fuel combustion, by reducing other activity that generates greenhouse gases, by averting venting of greenhouse gases to the atmosphere, and by recovering greenhouse gases from the atmosphere, for example in the form of enhanced biomass and soil carbon. Over one-third of Minnesota CO₂ emissions are derived from stationary sources such as coal-fired electrical generating stations and ethanol plants, and technology is now available to capture CO₂ from these sources. The likely fate of the captured CO₂, should this occur, would be storage by geologic sequestration, also known as carbon capture and storage (CCS), either by injection into deep saline underground geologic formations, or by mineral carbonation, which is reaction of CO₂ with mineral material to produce a benign solid product.

A conceivable deep injection option for Minnesota is export of CO₂ by pipeline to one or more potentially willing jurisdictions such as North Dakota or Illinois, where apparently suitable geologic repositories have been confirmed. It is possible, however, that saline formations in Minnesota could be confirmed as geologic CO₂ repositories, possibly enabling carbon storage by deep injection without the requirement for negotiations with neighboring jurisdictions and export by pipeline. The only rocks in Minnesota that potentially have the required reservoir properties below about a kilometer depth, the depth required for efficient CO₂ storage, are sequences of sedimentary rocks associated with the Midcontinent Rift, a southwestward extension of the Lake Superior basin that extends to Kansas. Criteria for confirmation of geologic potential include depth, porosity, permeability, presence of a seal, integrity relative to previous drilling or fractures, appropriate chemistry relative to lack of drinking water potential and chemical trapping mechanisms, and adequate data availability.

A report produced by Minnesota Geological Survey (Thorleifson, 2008) on the potential for deep injection of CO₂ in Minnesota reported that geophysical surveys summarized by Chandler (2008), including seismic, gravity and magnetic methods, indicate that the prospective rocks have depths and volumes compatible with sequestration of CO₂ in two north-south belts averaging about 40 km wide on either side of the Twin Cities, running from Pine County and Washington County south to Iowa. Required information on porosity and permeability is inadequately established from geophysical surveys, however, while limited information on lithostratigraphy, history, properties, and hydrogeology summarized by Runkel and Alexander (2008) indicates that these rocks have attributes that make them far less suitable for sequestration than sites being considered elsewhere. Positive attributes include some promising porosity and permeability values at shallow depths, presence of shales that could act as seals, and lack of previous deep exploration that would have left previous drillholes of varying integrity that could present a risk for leakage. On the negative side of the consideration, however, limited deep drillhole data indicate that sandstone at the depth required for sequestration, where measured, has porosity and permeability that are too low for injection of CO₂, while the seals have undergone a complex tectonic history that may have compromised their integrity.

The report thus concluded that available data indicate that there is a very low probability of success in confirming suitable geologic conditions for deep geologic sequestration of CO₂ in Minnesota, although it was acknowledged that these same data are inadequate to rule out the most prospective rocks. The report recommended that if further assessment becomes warranted, a comprehensive investigation encompassing geophysical surveys, multiple deep and thoroughly analyzed exploratory boreholes, followed by stratigraphic, structural, tectonic and hydrogeologic interpretation will be necessary to bring the understanding of these rocks up to a level analogous to that attained in areas where sequestration is being implemented on a test basis. This

first phase would cost tens of millions of dollars in the case of drilling of multiple sites. Preliminary aspects of this work are now going ahead at the Minnesota Geological Survey, at a modest pace, beginning with clarification of the depth and thickness of the prospective rocks through enhanced geophysical interpretations.

An additional recommendation provided by the 2008 Minnesota Geological Survey report was further analysis of the mineral carbonation option. In this method, CO₂ is reacted with material such as magnesium or calcium-bearing silicate minerals such as olivine and its alteration product serpentine to form geologically stable, environmentally benign carbonate minerals and quartz, allowing for the storage of CO₂ in a stable, inert and solid form without the need for burial or monitoring. A factor supporting this recommendation was the presence of large tonnages of appropriate rock material near Duluth that could potentially be mined for copper, nickel, and platinum group elements, in proximity to well developed infrastructure including major CO₂ sources. Should these deposits go into production, a slurry of minerals produced as a waste product from the potential mines could possibly be suitable for mineral carbonation of CO₂, and in a future scenario in which constraints are placed on CO₂ emissions, mineral carbonation could offer these mines another source of revenue.

The principal constraint to mineral carbonation at present, however, appears to be cost. An Intergovernmental Panel on Climate Change (IPCC) report by Sims et al. (2007) indicated that costs for deep injection of CO₂ into saline formations were estimated at the time to be 0.5 to 8 US\$/t CO₂, while their estimate for mineral carbonation, depending on the mineral and pretreatment used, was 50 to 100 US\$/t CO₂. The cost of mining and fine grinding was, however, included in this latter cost estimate, and this is a cost that mines would to some extent incur in any scenario. Commentary also has noted that the costs of long-term monitoring of deep injection sites may not have been fully accounted for. Furthermore, jurisdictions with mineral carbonation potential may wish to be prepared for developments in the mineral carbonation method leading to cost reductions. In addition, there could be circumstances in which a particularly favorable mineral carbonation opportunity coincides with constraints to other sequestration options, such as transportation, thus possibly making mineral carbonation a conceivable option. The State of Minnesota, through the Minnesota Minerals Coordinating Committee (MCC), therefore commissioned the current report, a literature review on the potential for implementation of mineral carbonation as a carbon sequestration method in Minnesota, to clarify considerations, and to very roughly determine the potential magnitude of the opportunity.

Mineral carbonation involves reaction of CO₂ with metal-oxide bearing materials, either abundantly available natural silicate minerals such as olivine, or alkaline industrial wastes such as ash or slag, thus forming benign solid carbonate and silica. The reaction is exothermic and can therefore theoretically yield energy, but the process is slow, so energy intensive preparation such as fine grinding is needed, resulting in a cost of ~\$54US/t CO₂, in the case of near-pure olivine, including the cost of mining and fine grinding, although research on cost reduction is ongoing. The mineral carbonation method remains in its infancy, however, with no full-scale demonstration in place. Nevertheless, the method remains somewhat promising, due to slow deployment of deep injection, the great abundance of suitable minerals, steady progress on methods, the ability to treat gases without expensive separation of CO₂, potentially favorable thermodynamics, potentially usable products, and lack of leakage risk or monitoring requirements.

Olivine and serpentine, the minerals favored in scenarios for mineral carbonation of CO₂, occur most abundantly in ultramafic rocks, which are those richest in olivine and serpentine, as well as in mafic rocks, in which the desired minerals are diluted with feldspar due to a higher silica content. Scattered, typically deeply buried ultramafic rocks occur across Minnesota. Much more abundant and accessible, however, are the large deposits of mafic rocks of the Duluth Complex and its satellites, an extensive complex of gabbro and related mafic rocks along and inland from the north shore of Lake Superior, from Duluth to Babbitt to the Ontario border. The most likely initial mineral carbonation implementation scenario, it seems, would be use of mining wastes, rather than mining for this purpose, due to lower costs and potentially simpler implementation. There are no existing olivine or serpentine-bearing mine wastes in Minnesota, so implementation scenarios for Minnesota correlate to

scenarios for future mining of mafic and ultramafic rocks. While no advanced exploration projects exist in Minnesota ultramafic rocks, the Duluth Complex includes multiple exploration programs, some at advanced stages. This report therefore focuses on the potential for mineral carbonation utilizing wastes from one or more already-proposed or readily-conceivable future mines in the Duluth Complex – none of which are as yet permitted pending environmental review and other considerations – although the concepts are applicable to any future ultramafic mining scenario.

The Duluth Complex and associated intrusions are one of the largest mafic intrusive complexes in the world, covering an area of over 5,000 square km. The Complex is divisible into multiple series and intrusions. Mineral deposits in the western Duluth Complex constituting billion of tons of material bearing copper, nickel, titanium, and platinum group elements (PGE) have been described since the 1960s. Additional mafic rocks occur closer to Lake Superior in the Beaver Bay Complex. A satellite of the Duluth Complex is the Tamarack ultramafic intrusion located 80 km west of Duluth. Exploration activity by multiple parties is currently underway at multiple properties in the Duluth Complex. An indication of the presently conceived character and scope of potential mining in the Duluth Complex is provided by the PolyMet Mining Inc./NorthMet Project draft Environmental Impact Statement, which proposes mining of up to 32,000 tons per day of ore over an approximately 20-year mine life – should this proposed mine go ahead.

Use of future olivine-bearing mining wastes thus seems the most plausible potential initial scenario for implementation of the method in Minnesota, as one or more potential mines near Duluth could produce abundant olivine and serpentine-bearing material as a waste. A CO₂ source could be a present or future electrical generating station. The current mining proposal that anticipates production of 32,000 tons per day of ore would likely be producing wastes that would consist of one-third olivine that might not be significantly serpentinized, so the mine would be producing over 10,000 tonnes per day of crushed olivine. At the efficiency of 80% indicated by research on the method, and if serpentinization turns out not to be significant, this olivine could be used to sequester something on the order of 1.9 million tonnes of CO₂ per year, about 1% of the CO₂ produced in Minnesota. Serpentinization more extensive than anticipated would degrade potential for mineral carbonation.

The published cost estimate for mineral carbonation using olivine, \$54US/t CO₂, includes the cost of mining and processing, but in the scenario outlined here, additional size reduction would be required beyond that needed by the mine, and there may be other costs such as serpentine treatment, and inefficiency related to an olivine content less than the near-pure olivine that this cost estimate was based on, so no cost reduction is assumed. In addition, no costs for CO₂ acquisition are assumed. On this basis, the carbon storage would cost about 100 million dollars per year, and the carbonation business unit would presumably need to anticipate some form of carbon credits and/or regulatory incentives adequate to justify this cost. The dissolved olivine would contain a significant quantity of nickel, which potentially could be recovered and sold in return for revenue, however, although recovery viability, efficiency, and costs are undetermined. The carbonation circuit would increase the volume of solid wastes produced by the mine by about a half or more, and whether the produced carbonate could play a role in mitigating potential acid mine drainage is unclear.

Mines in Minnesota thus may soon produce large quantities of olivine that could be used to sequester CO₂, although costs quite possibly exceeding \$50US/t CO₂ are a likely barrier. Incentives, cost reductions, or metal production from the mineral carbonation procedure could, however, justify implementation. One mine at currently foreseen scales could sequester about 1% of Minnesota's CO₂ emissions, at a cost of about 100 million dollars per year less any credits for produced metals, if the incentives relative to cost somehow become favorable. Sequestration of a higher proportion of our CO₂ by this method would require some combination of higher production rates, more than one mine, or preferential mining of olivine.

INTRODUCTION

Minnesota, with a population of about five million, is a significant source of greenhouse gas emissions (Strait et al., 2007), and a state that is vulnerable to climate change, such as the impact that increased frequency or severity of drought or storms would have on agriculture, water supply, wildlife, lake levels, and public security. Minnesota therefore has an interest in reducing our own vulnerability, while concurrently contributing to needed world-wide solutions. As has been stressed, for example, in documents prepared for and by the Minnesota Climate Change Advisory Group, emissions reductions can have multiple benefits, including conservation, cost efficiency, and air quality enhancement, while also directly contributing to mitigation of climate change. Anthropogenic climate change seems already to have begun (Solomon et al., 2007), however, so adaptation to climate change accompanies mitigation in the climate change policy agenda. Mitigation of greenhouse gas emissions can be achieved through reduced fossil fuel combustion, while concurrently capturing and storing carbon in biomass, or in geologic repositories (Metz et al, 2007). It has become apparent that the best approach is likely to be for several options to concurrently be implemented (Pacala and Socolow, 2004).

Minnesota may be well positioned to utilize the mineral carbonation method of geologic carbon sequestration, given the presence of vast tonnages of appropriate rock material in the Duluth region, some of which could be mined for copper, nickel, and platinum group elements, pending the outcome of current permitting procedures. Should these deposits go into production, a slurry of minerals suitable for mineral carbonation of CO₂ would be produced as a waste product from the mines. The principal constraint to mineral carbonation at present appears to be cost. Nevertheless, there could be developments in the method, and there could be circumstances in which a particularly favorable mineral carbonation opportunity could coincide with constraints to other aspects of the sequestration procedure, such as considerations regarding transportation, thus possibly making mineral carbonation a conceivable option.

MINERAL CARBONATION

Mazzotti (2005) defined the mineral carbonation sequestration method as reaction of captured CO₂ with metal-oxide bearing materials, either abundantly available natural silicate minerals such as olivine, or alkaline industrial wastes such as ash or slag, thus forming stable carbonates and a solid byproduct such as silica. In nature, mineral carbonation is called silicate weathering, and the process involves liberating cations to neutralize carbonic acid. The reaction is exothermic and thus can theoretically yield energy, but the process is slow, so energy intensive procedures such as preparation of the material through fine grinding are needed.

The potential to use the mineral carbonation reaction to achieve greenhouse gas mitigation was first proposed by Seifritz (1990) and Dunsmore (1992). Much detail on implementation scenarios was subsequently provided by Lackner et al. (1995; 1997; 1998), and later by Zevenhoven and Kohlmann (2001), Lackner (2002; 2003), and Herzog (2002). The method was also broadly discussed by Inui (1996) and by Xiaoding and Moulijn (1996). The currently favored process was developed by the US Department of Energy (DOE) National Energy Technology Laboratory (NETL) in Albany, Oregon (O'Connor et al., 1999; 2000; 2001; 2002; 2005). Building on this process, acceleration of the method was broadly addressed by Goldberg et al. (2001) and by Gerdemann et al. (2003; 2004), while environmental considerations in general were examined by Haywood et al. (2001). Comprehensive reviews of mineral carbonation as a carbon storage method have been provided by Huijgen and Comans (2003; 2007b), Mazzotti (2005), Oelkers et al. (2008), Sipilä et al. (2008), Stephens and Keith (2008), as well as Zevenhoven et al. (2011). Currently contemplated reaction processes were summarized by Zevenhoven and Fagerlund (2010).

Olivine-rich rocks may also permit *in situ* mineral carbonation (Oelkers et al., 2008; Kelemen and Matter, 2008; Matter and Kelemen, 2009), in which CO₂ is injected through drillholes of moderate depth into the rock where it

reacts with olivine and other minerals if adequate permeability is present or can be induced. Rocks that lack the significant porosity and permeability that may be present for example in the case of modern volcanic rocks, or in which it is not practical to induce permeability, would preempt injection, so in this case mining of the appropriate minerals would be foreseen, followed by *ex situ* mineral carbonation in a process plant.

In the *ex situ* method, according to Mazzotti (2005), captured CO₂ is reacted with metal-oxide bearing materials, thus forming stable solids that would provide secure storage on a geological time scale. Moreover, it was suggested, magnesium and calcium silicate deposits are so vast in their availability that CO₂ resulting from combustion of all known fossil fuels resources could be sequestered. Mazzotti (2005) indicated that to fix a tonne of CO₂ requires about 1.6 to 3.7 tonnes of rock, with olivine being most favorable, and that, from a thermodynamic viewpoint, inorganic carbonates represent a lower energy state than CO₂ so the reaction theoretically could yield energy. The kinetics of natural mineral carbonation are slow, however, so it was indicated that all currently implemented processes require energy intensive preparation of the solid reactants, such as grinding and heat treatment, to achieve affordable conversion rates, and/or additives that must be regenerated and recycled using external energy sources. The resulting solids must be stored at an environmentally suitable location, such as refilling of an open pit mine. It was indicated that the technology is still in the development stage and is not yet ready for implementation, although the best case studied was said to be wet carbonation of olivine, costing 50 to 100 US\$/t CO₂ stored, including the cost of mining and grinding.

Mazzotti (2005) indicated that metal oxides are being favored rather than alkali metals such as sodium and potassium, as the latter result in carbonates that are very soluble in water. It was further noted that oxides and hydroxides of calcium and magnesium would be ideal, but they are rare in nature. The best source of serpentine and olivine are mafic and ultramafic rocks, while wollastonite is less abundant. In addition, it was noted that mineral carbonation feedstocks could produce marketable metals such as nickel as byproducts of the carbonation process, as further discussed by Goff et al. (1997; 2000). Use of existing stored wastes for mineral carbonation has also been discussed (Doria, 2005; Wilson et al. 2006; 2009; Dipple et al., 2008; Hitch et al., 2010; Krevor et al., 2009a; b; Wilson et al, 2010).

The review by Mazzotti (2005) indicates that olivine is most favorable because it has the highest concentration of reactive magnesium oxide, 57% by weight, among the natural minerals. The review further indicated that for pure serpentine, the magnesium oxide concentration is about 44%. The stoichiometry of the carbonation reaction indicates that 1.6 tonnes of olivine would be needed to fix one tonne of CO₂, thus producing 2.6 tonnes of solid material for disposal. Assuming 90% carbonation conversion and 10% losses in the classifier, 1.62 tonnes of olivine would be needed and 2.62 tonnes of solids per tonne of CO₂ mineralized would be for disposal. Assuming only 50% conversion and 20% losses, for one tonne of CO₂ stored, 1.87 tonnes of olivine would be needed and 2.87 tonnes would be disposed of. Therefore, the mineral feedstock required to fix 1 tonne of CO₂ in carbonates is between 1.6 and 3.7 tonnes and the process yields between 2.6 and 4.7 tonnes of products to be handled. Finally, the review by Mazzotti (2005) indicated that the carbonation process consumes energy, with the lowest energy requirement applying to reaction with olivine - 1.1 GJ/t CO₂, and if this energy is derived from coal, the process would cause CO₂ emissions equal to 30% of the fixed CO₂.

The amount of solid product to be disposed of is between 50 and 100% by volume more than that originally mined, which would be disposed of in tailings impoundments near the processing site (Lackner et al., 1997; Newall et al., 2000). It is estimated that storage of all carbon resulting from coal combustion by mineral carbonation would require a mining enterprise comparable in scale to coal mining itself (Mazzotti, 2005), or perhaps five times the scale of coal mining (Gerdemann et al., 2007), although in reality, a spectrum of storage methods seems a more likely scenario, in which mineral carbonation would be one of several methods.

Necessary mineral pretreatment would at least involve crushing, grinding, and milling, as well as some mechanical separation, for example magnetic extraction of magnetite, while little pre-processing or compression

of the CO₂ is required (Mazzotti, 2005). Reaction of gaseous CO₂ with solid particulate metal oxide is too slow to be practical at reasonable pressures, so extraction of the metal from the solid by dissolution is required, permitting reaction of metal ions such as magnesium or calcium with carbonic acid that is formed in the same solution upon CO₂ dissolution, followed by precipitation of products.

Efforts directed toward cost reduction have focused on acceleration of the reaction through enhanced metal oxide bearing material dissolution rate, reduction of interference between metal oxide dissolution and carbonate precipitation, and more efficient recovery of materials (Mazzotti, 2005). Accelerated dissolution may be achieved by making the material more labile and reactive through heat-treatment at 650°C for serpentine (O'Connor et al., 2000; McKelvy et al., 2004), physically activated dissolution of serpentine (Park and Fan, 2004), or fine grinding for olivine and wollastonite (O'Connor et al., 2002; Kim and Chung, 2002). Alternatively, dissolution can be enhanced by catalysts such as acids (Lackner et al., 1995; Fouda et al., 1996; Park et al., 2003; Maroto-Valer et al., 2005; Alexander et al., 2007; Teir et al., 2007b), bases (Blencoe et al., 2003), or chelating agents (Park et al., 2003), although catalyst recovery is a challenge (Mazzotti, 2005). Carbonate precipitation has been addressed by Hänchen et al. (2008), magnesium hydroxide production from serpentine was discussed by Fagerlund et al. (2009), the issue of a rate-limiting reaction product layer was examined by Butt et al. (1996) and Jarvis et al. (2009), while Prigiobbe et al. (2009a) examined olivine dissolution. Munz et al. (2009) examined optimization of magnesite and silica products, in relation to the potential for commercially viable outputs. In investigating the production of hydromagnesite from serpentinite, Teir et al. (2009) found that the process requires recycling of large amounts of sodium hydroxide and acid, and was thus more expensive than available CO₂ storage options, although they found that the process studied might be suitable for producing valuable mineral and metal products from serpentinite.

Research is clarifying optimal temperature and pH for the mineral carbonation reaction. Temperature affects the solubility of CO₂ and the rate of mineral dissolution in opposing fashions, and investigations have found that an optimum temperature for carbonation of olivine is ~185°C and ~155°C for serpentine (Gerdemann et al., 2003). With respect to pH, if leaching magnesium silicate and forming magnesium carbonate occur in the same reactor, lowering the pH helps dissolve magnesium ions from silicate, but it lowers carbonic ion concentration and limits precipitation of magnesite, so a balance is needed (Chen et al., 2006); an option is to separate the processes (Teir et al., 2007a).

Newall et al. (2000) estimated an overall mineral carbonation cost of 80 US\$/t CO₂ stored, with 27.5% additional CO₂ emissions, thus leading to 110 US\$/t CO₂ avoided, while for another method Kakizawa et al. (2001) estimated an overall cost of 27 US\$/t CO₂ avoided. According to Mazzotti (2005), however, O'Connor et al. (2005) achieved a more comprehensive energy and economic evaluation, indicating storage costs of \$54 US\$/t CO₂ for near-pure olivine, with higher costs for more finely ground olivine, and still higher costs being estimated for serpentine or wollastonite.

The lowest cost estimate for serpentine produced by O'Connor et al. (2005) was \$78 US\$/t CO₂ for the antigorite form of serpentine when finely ground, with much higher costs in some cases exceeding \$400 US\$/t CO₂ for the lizardite form of serpentine. This analysis clearly favored olivine from a cost point of view, and called into question the viability of serpentine usage.

These published cost scenarios include the cost of mining and grinding, with grinding making up the majority of energy costs (O'Connor et al., 2005). A scenario in which a mineral carbonation business unit receives ground olivine and/or serpentine at no cost, or is paid to receive the material, would thus involve costs of something less than ~\$54US/t CO₂ stored. Furthermore, commercial byproducts derived from the mineral carbonation process, such as nickel from olivine, would be a consideration in the commercial viability of the process.

Once the carbon has been stored through mineral carbonation, there are virtually no emissions of CO₂ due to leakage, and the need for monitoring the disposal sites will be negligible (Mazzotti, 2005). In addition, Allen and Brent (2010) demonstrated that a worst-case scenario for acid rain resulted in negligible CO₂ release from hypothetical mineral carbonation products. Viability of implementation will require an economic life cycle evaluation of CO₂ recovery as well as mineral use and sequestration alternatives (Khoo and Tan, 2006; Zevenhoven et al., 2006; Huijgen et al., 2007, 2007b), while doubts have been expressed on the viability of the method, at least for broad implementation, by Gerdemann et al. (2007) and IEA (2008). Public acceptance of the method likely will focus on mining, so in cases where mining has been justified by other means, likelihood of acceptance of mineral carbonation may be high, as the integrity of the process is highly verifiable, while secure long-term storage is assured, with minimal monitoring requirements (Mazzotti, 2005).

With respect to recent perception of the potential that the method offers, Sipilä et al. (2008) outlined that mineral sequestration for the long-term storage of CO₂ is an alternative to deep injection that is most suitable for areas lacking reservoir capacity, where risk of leakage is unacceptable, or where large resources of material suitable for carbonation are present. They pointed out that although the method remains too slow and expensive, research is rapidly accelerating due to its vast capacity, its lack of leakage risk or need for post-storage monitoring, and the theoretical potential to harness its potentially favorable thermodynamics. They noted that aqueous solutions remain the preferred medium for the reaction, either direct methods involving an additive that drives the reaction rate, or indirect methods where extraction of Mg or Ca and their subsequent carbonation are separate steps. They concluded that for large-scale operations using magnesium silicates, costs using an aqueous method would exceed 40 €/t CO₂ (~\$55US/t CO₂), while they also stressed the importance of ongoing work on stepwise carbonation of serpentine with the exothermic carbonation step conducted at high temperatures and pressures.

Prigobbe et al. (2009b) also reiterated that the most promising method remains an aqueous process using olivine, serpentine, or wollastonite, followed by precipitation of carbonates such as magnesite and calcite, and they reported experiments to investigate both the dissolution and the precipitation processes. Krevor and Lackner (2009) deemed the lowest cost available option to be direct carbonation of a slurry of magnesium or calcium silicate mineral with supercritical CO₂, in a process limited by the slow reaction kinetics of the carbonation reactions, and in particular the slow dissolution rates of the silicates in weakly acidic conditions. They noted that serpentine due to its reactivity and abundance is prospective, and they presented results of experiments on enhanced dissolution of serpentine at 120°C and under 20 bars of CO₂.

Teir et al. (2010) concluded that for large-scale CO₂ mineralisation of magnesium silicates, the best option remains the Albany process (O'Connor et al., 1999; 2000; 2001; 2002; 2005), involving a slurry of water and pretreated mineral reacted with pressurised CO₂ (40–150 bar) at a temperature of 100–185°C to produce magnesium carbonate and silica.

Most recently, Zevenhoven et al. (2011), stressed that the years ahead will show whether CO₂ mineral sequestration can be demonstrated, perhaps at a level of 1 Mt/a CO₂ by the year 2020. They indicated this demonstration may occur, due to slow deployment of deep injection, the great abundance of suitable minerals, steady progress on methods, lack of leakage risk and monitoring requirements, potentially usable products, and potentially favorable thermodynamics. In addition, they noted, a recently recognized advantage is the ability to treat gases without expensive separation of CO₂. Finally, they noted that current developments include an increasing number of patents and patent applications, and a trend toward scale-up and demonstration.

In summary, the mineral carbonation method remains in its infancy, with no demonstration in place, and further progress needed to reduce costs and energy requirements, and to demonstrate integrated power generation, mining, transportation of materials and energy, carbonation reaction, and disposal (Mazzotti, 2005).

SOURCES OF REQUIRED MATERIALS IN MINNESOTA

Olivine and serpentine, the minerals favored in scenarios for mineral carbonation of CO₂, occur most abundantly in ultramafic and mafic rocks. Krevor et al. (2009a; b), in producing an inventory of rocks in the US that are most suitable for mineral carbonation, thus focused on ultramafic rocks. They outlined extensive deposits in the states of California, Oregon, and Washington, scattered occurrences in Minnesota and Wisconsin, and significant deposits extending from Georgia to Maine, with a few sites in intervening areas. For data on ultramafic rocks in Minnesota, Krevor et al. (2009a; b) relied on a recent data release compiled by the Minnesota Geological Survey for the purpose of mapping rocks with potential for platinum group elements (PGE) (Jirsa et al., 2006). On this basis, Krevor et al. (2009a; b) drew attention to scattered small occurrences of ultramafic rocks across Minnesota, most deeply buried under glacial sediments. Abundant, accessible, and much more extensive deposits rich in olivine and serpentine also occur, however, in the Duluth Complex and its satellites, an extensive complex of gabbro and related mafic rocks along and inland from the north shore of Lake Superior, from Duluth to Babbitt to the Ontario border (Jirsa et al., 2011).

Two scenarios can be considered for mineral carbonation using natural silicates – mining conducted for this purpose alone, or use of wastes from mining. The latter could involve use of wastes as they are produced, or use of wastes stored at a producing or past-producing mine. Research to date in the mineral carbonation field has focused on mining for the purpose of carbonation, or the use of large waste stockpiles. By taking this approach, scenarios for large-scale implementation relevant to the long-term were considered.

It seems, however, that the most likely initial implementation scenario for mineral carbonation would be use of finely ground mining wastes as they are produced. This would be due to regulatory requirements for mining having already been satisfied, and lowest overall cost of material acquisition. This would be analogous to the suggestion that deep injection of CO₂ for the purpose of sequestration will first be undertaken where there are commercial benefits in the form of enhanced oil recovery, a well-established oilfield method that uses CO₂.

If use of mining waste is likely to be the first phase of mineral carbonation implementation, should it occur, it can next be noted that there are no existing olivine or serpentine-bearing mine wastes in Minnesota. Implementation scenarios for Minnesota thus seem most likely to correlate to scenarios for future mining of mafic and ultramafic rocks. Although, as it has been noted, there are ultramafic rocks at scattered sites across Minnesota, some of which have been drilled, none of these sites constitutes an advanced exploration project. In contrast, the Duluth Complex represents a resource of olivine and serpentine that is not only vast and well exposed, it also includes multiple exploration programs, some at advanced stages.

This report therefore will focus on the potential for mineral carbonation utilizing wastes from one or more already-proposed or readily-conceivable potential future mines in the Duluth Complex. Should a future mining scenario emerge for an ultramafic rock body in Minnesota, however, the concepts discussed here would be readily applicable to that case. A mafic rock, for the purpose of this discussion, can be regarded as being identical to ultramafic rocks, with the inclusion of slightly higher silica content, and thus more feldspar.

DULUTH COMPLEX

According to Miller and Ripley (1996), and later Miller and Severson (2002), the Duluth Complex and associated intrusions constitute one of the largest mafic intrusive complexes in the world, covering an area of over 5,000 square km. The earliest documentation of the Duluth Complex was by Winchell (1899), while further studies were reported by Grout et al. (1959), Taylor (1964), Bonnicksen (1972a; 1972b; 1974a), and by Davidson (1972). Reviews and additional contributions were then reported by Weiblen and Morey (1980), Weiblen (1982), Green (1986), Chandler (1990), Miller and Weiblen (1990), as well as Paces and Miller (1993).

According to Miller and Severson (2002), the Duluth Complex is divisible into felsic series, early gabbro series, anorthositic series, and layered series, including layered series at Duluth, as well as the Boulder Lake intrusion, the Western Margin intrusion, the Partridge River intrusion, the South Kawishiwi intrusion, the Lake One troctolite, the Tuscarora intrusion, the Wilder Lake intrusion, the Bald Eagle intrusion, the Greenwood Lake intrusion, and finally the Osier Lake intrusion.

Additional mafic rocks occur closer to Lake Superior, in the Beaver Bay Complex (Miller and Green, 2002), including the Sonju Lake Intrusion (Maes et al., 2007; Stevenson, 1974; Miller et al., 1993; Miller and Ripley, 1996; Miller and Chandler, 1997; Miller, 1999; Joslin and Miller, 2003; Joslin, 2004; Park et al., 2004). A satellite of the Duluth Complex first described by Southwick et al. (1986) is the Tamarack ultramafic intrusion located 80 km west of Duluth that has recently been described by Goldner (2011a; 2011b).

MINERAL DEPOSITS

Mineral deposits in the western Duluth Complex, bearing copper, nickel, titanium, and platinum group elements (PGE), were first described by Sims (1968), Bonnicksen (1972b; 1974b), Boucher (1975), as well as by Hauck et al. (1997). Severson et al. (2002) noted occurrences of disseminated copper-nickel-PGE-sulfide mineralization in the ~100 m thick basal contact zones of the mafic intrusions, and massive sulfide mineralization at the basal intrusive contact and in underlying rocks. The disseminated sulfide mineralization occurrences were described as large resources of low-grade copper-nickel sulfide ore that locally contain anomalous PGE concentrations. For example, they outlined nine disseminated sulfide deposits that they estimated to constitute over 4.4 billion tons of material averaging 0.66 percent copper and 0.2 percent nickel, using data by Listerud and Meineke (1977).

Research on Duluth Complex mineral deposit characterization and the processes of mineralization was reported by Mainwaring and Naldrett (1977), Churchill (1978), Bonnicksen et al. (1980), Grant and Molling (1981), Ripley (1981), Rao and Ripley (1983), Pasteris (1984), Tyson and Chang (1984), Ripley (1986), Ripley and Alawi (1986), Chalokwu and Grant (1987), Ripley and Al-Jassar (1987), Ripley and Alawi (1988), Andrews and Ripley (1989), Chandler and Ferderer (1989), Chalokwu and Grant (1990), Ripley (1990; 1990b), Mogessie et al., (1991), Ripley et al. (1993), and by Ripley and Chryssoulis (1994).

The most recent research on the mineralization has examined interaction with basaltic magma (Arcuri et al., 1998), liquid immiscibility (Ripley et al., 1998a), mantle and crustal contributions to magmatic sulfide mineralization in the Duluth Complex (Ripley et al., 1998b), interaction of the rocks with those into which they were emplaced (Ripley et al., 2007), as well as mineralization styles and magmatic and hydrothermal processes (Gál et al., 2011).

In addition, mineral potential assessments have examined specific intrusions, such as the Greenwood Lake intrusion (Miller, 2004), the Partridge River Intrusion (Severson and Hauck, 1990; Severson, 1991; Patelke, 1996; Severson and Hauck, 1997; Thériault et al., 2000), the South Kawishiwi intrusion (Severson, 1994), and the South Complex later renamed the Western Margin intrusion and the Boulder Lake intrusion (Severson, 1995). Additional investigations examined the rocks on which the Duluth Complex was emplaced (Peterson and Severson, 2002), as well as associated volcanic and sedimentary rocks (Green, 2002). A history of copper-nickel and titanium oxide test pits, bulk samples, and related metallurgical testing in the Duluth Complex was provided by Patelke and Severson (2005).

According to Goldner (2011a; 2011b), the Tamarack intrusion is about 13 km long and from 1 and 4 km wide, and while the narrow end is exclusively ultramafic, largely feldspathic lherzolite, the wider end trends toward more mafic rocks. Disseminated Ni-Cu-PGE sulfide mineralization was reported to be in greatest abundance in a narrow tail area of the intrusion. With respect to characterization of these minerals, Goldner (2011a; 2011b), for

example, has indicated olivine compositions ranging from 84% forsterite, the magnesium end-member as opposed to the iron end-member, in the lowermost ultramafic rocks, to 10% forsterite in the mafic rocks. Although the rocks commonly consist of 40 to 80% olivine, the rocks were described to be variably but significantly serpentinized, with loss on ignition values ranging up to 15%. A significant nickel concentration in these olivine-rich, or formerly olivine-rich serpentinized rocks, was indicated by NiO levels of about 0.25%.

CURRENT EXPLORATION ACTIVITY

Current exploration activity by multiple parties is best described in company press releases and web sites, news coverage, and information provided by the Minnesota Department of Natural Resources (DNR). In addition, the Precambrian Research Center (PRC) and the Natural Resources Research Institute (NRRI) of the University of Minnesota Duluth have provided syntheses of current exploration activity at several properties.

MINING SCENARIOS

An indication of the character and scope of potential mining in the Duluth Complex is provided by the PolyMet Mining Inc./NorthMet Project draft Environmental Impact Statement, currently available on the web site of the DNR. These documents indicate that the NorthMet Project would involve mining and mineral processing of approximately 228 million tons of Cu-Ni-PGE ore over an approximately 20-year mine life, and that PolyMet proposes to open-pit mine an average of approximately 91,200 tons per day (tpd) of rock, including up to 32,000 tpd of ore.

MINERAL CARBONATION SCENARIOS

Conceivable scenarios for implementation of mineral carbonation as a climate change mitigation method in Minnesota are here considered. Research on mineral carbonation summarized in this report, in particular the analyses by O'Connor et al. (2005) and Gerdemann et al. (2007), has strongly favored appropriately ground olivine, and to a lesser extent serpentine, as the best feedstock for the method. This research indicated that for near-pure olivine, size reduction to 80% minus 400 mesh or 37 microns resulted in a minimized cost of \$54 US\$/t CO₂ reacted, whereas coarser pretreatment at 75 microns resulted in a much lesser degree of reaction, while finer sizes increased cost per tonne of CO₂. The work indicated that serpentine would require heat pretreatment, resulting in costs no less than \$78 US\$/t CO₂, with higher and likely prohibitive costs for some forms of serpentine.

Use of future mining wastes seems the most plausible potential initial scenario for implementation of the method in Minnesota, as costs and implementation would be more favorable than dedicated mining. No existing usable wastes exist in the state, so future mining is at present considered the most conceivable scenario for implementation. Although mineral potential exists in scattered very-olivine-and/or-serpentine-rich ultramafic rocks in Minnesota, mineral production at present seems much more likely in the form of proposed and potential nickel, copper, and platinum-group-element (PGE) mining in Duluth Complex mafic rocks, which are only slightly less rich in olivine and serpentine than the ultramafic rocks. One or more mines in the Duluth Complex and its satellites could recover sulfide minerals for the purpose of economic metal recovery, while producing olivine and/or serpentine-bearing material as a waste.

A scenario for mineral carbonation in Minnesota can thus be constructed on the basis of availability of suitable and adequate CO₂, tons per day of ore processed and thus waste produced after accounting for ore minerals retained, the percentage of the ore consisting of olivine and/or serpentine, the ratio and character of these minerals, the effectiveness of these minerals in reacting with CO₂, the cost of the process per tonne of CO₂, the economic and/or regulatory factors that might influence the CO₂ storage, and the commercially valuable materials that could be produced as a byproduct of the process.

A CO₂ source could be a present or future electrical generating station on the Iron Range, Duluth, or on the North Shore. A regulatory filing by Excelsior Energy Inc. dated October 10, 2006, for example, outlined a proposed new electrical generating station on the Range, for which one option was to incorporate a CO₂ pipeline to North Dakota, with storage of CO₂ in oil fields or saline formations.

In the potentially conceivable scenario sketched here, a CO₂ producer might pay the mineral carbonation business unit to receive CO₂, as a result of a regulatory obligation or incentive, the CO₂ could arrive without cost due to a mutually beneficial agreement, or perhaps the mineral carbonation unit would purchase the CO₂. Which of these scenarios is most likely to prevail would depend on the set of policies in place at the time.

The current mining proposal for the Duluth region described in this report anticipates production of 32,000 tons per day of ore, and this could possibly be the first of more than one mine, according to research summarized here, as well as company press releases and industry news reports. The sulfide minerals recovered in order to produce nickel, copper, and PGE would be of negligible weight, according to the proposal and research on these rocks, so the mine would be producing close to 32,000 tonnes per day of silicate, oxide, and other minerals.

A topic of considerable significance to the potential for mineral carbonation in this area is the degree of serpentinization of olivine in these deposits, as serpentine is considerably less desirable and more costly as a feedstock for mineralization, for example due to the need for heat treatment in some cases. Although considerably more information would be needed to better clarify this issue, current indications are that the olivine of the Duluth Complex deposits is quite variably serpentinized. White (2010), as well as Marma (2004), Williams et al. (2010), and Gál et al. (2011), for example, indicate that while subtle serpentinization is omnipresent in the rocks they studied, it is localized, and variable where present, ranging from thin veinlets to heavily serpentinized olivine grains. The PolyMet Mining Inc./NorthMet Project draft Environmental Impact Statement, however, notes a lack of fibrous serpentine in the rocks. These reports therefore seem to imply that a minority of the olivine is serpentinized, and that it can be anticipated that while some deposits would be insignificantly serpentinized, others would likely be heavily serpentinized. Any future indications that serpentinization is more extensive than this would degrade mineral carbonation potential.

Having noted the importance and significance of serpentinization, it is now noted that literature summarized in this report indicates that the ore in the Duluth Complex would tend to be about one-third olivine, so a mine operating on the scale indicated by the first proposal would be producing over 10,000 tonnes per day of olivine.

For the PolyMet Mining Inc./NorthMet proposal, however, the ore would only be reduced to 120 microns, so further size reduction would be needed for the purpose of mineral carbonation. For olivine, the currently available cost estimate for mineral carbonation of \$54 US\$/t CO₂ includes the cost of mining and size reduction to 37 microns. For the scenario outlined here, costs would be lessened if the mineral carbonation unit did not incur mining costs, although additional costs would be incurred for size reduction, if serpentine is a factor, and also given that the ore described here is only one-third olivine, presumably resulting in inefficiencies relative to the more ideal scenarios described in published research. The relevance if any of Mg/Fe ratios in olivine also is not considered. Therefore, no cost savings in relation to mining costs are assumed here, and for the purpose of this discussion, a cost of \$54 US\$/t CO₂ will be assumed as a basis for a preliminary calculation.

Literature on the method can be used as a guide to infer that if only the olivine reacts with CO₂, and if eight-tenths of the olivine reacts, this scenario would involve sequestration of about 5300 tonnes of CO₂ per day, and thus about 1.9 million tonnes of CO₂ per year, about 1% of the CO₂ produced in Minnesota. Using the cost estimate of \$54US/t CO₂ stored, this carbon storage would cost about 100 million dollars per year. Depending on the basis by which the CO₂ and olivine are received, the carbonation business unit would presumably need to anticipate some form of revenue due to carbon credits and/or regulatory incentives adequate to justify this cost.

If the olivine consists of 0.1% NiO, however, as indicated as being possible by research in the region, there is a potential for additional revenue to be derived from this and potentially other metals that would be brought into solution. Whether recovery of metals would be possible, however, and what additional costs would be incurred to do so, remains unstudied (Mazzotti, 2005).

The carbonation circuit would increase the volume of solid wastes produced by the mine by about a half or more. Given that abundant readily quarryable carbonate and silica resources are available in the region, it seems unlikely that the carbonate or quartz products could be marketed. Whether the produced carbonate could play a role in mitigating potential acid mine drainage also is unclear on the basis of the current very preliminary discussion.

CONCLUSIONS

Minnesota may soon host one or more mines producing large quantities of olivine in their waste. Although the mineral carbonation method has not been demonstrated at field scale, experimental results suggest that it is likely that this olivine, and possibly other minerals, could be used to sequester CO₂ in a stable solid form. At a cost quite possibly exceeding \$50US/t CO₂, however, costs are likely to present a large barrier. Implementation of the method would thus appear to be contingent upon incentives being adequate to cover this cost, unless cost reductions are achieved, or if metal production from the mineral carbonation procedure is a significant offset. It appears that one mine at currently foreseen scales could sequester about 1% of Minnesota's CO₂ emissions, at a cost of about 100 million dollars per year less any credits for produced metals, if the incentives relative to cost somehow become favorable. Current Minnesota goals, however, are to reduce state emissions 15% by 2015, 30% by 2025, and 80% by 2050. For sequestration by the mineral carbonation method of a proportion of our emissions larger than 1% to be contemplated, however, some combination of higher production rates, more than one mine, or preferential mining of olivine would have to be anticipated.

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