An Evaluation of Mineral

Carbonation as a Method for

Sequestration of Carbon Dioxide.

by

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ABSTRACT

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Abstract: During a period 55 million years ago, referred to as the Paleocene-Eocene thermal maximum, Earth's climate was 2^oC warmer than at present. Then an influx of atmospheric carbon dioxide raised Earth's temperature by another 5^oC. Earth's own negative feedback brought the carbon dioxide level and the temperature back to equilibrium over a period of 100,000 to 200,000 years.   Today, we again struggle with excess carbon dioxide in the atmosphere. The most obvious way to get rid of the excess is to store it in geological formations, such as empty gas and oil reservoirs, but they are likely to develop significant leaks. A process has been identified to further react the carbon atom of the carbon dioxide in order to totally neutralize it, using the same process as Earth had used. This method has been emulated in the laboratory and could be applied to carbon dioxide as it is generated by point source emitters such as power plants. Because the reaction products are solid, benign, common in nature, and insoluble in water, the carbon dioxide treated in this manner is permanently kept from entering the atmosphere and ocean, and produces no effect on the climate. While chemical reaction of the carbon dioxide costs more than pumping it into geologic formations, the environmental impacts are minimal because the storage is permanent without the possibility of leakage.

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INTRODUCTION

Since the beginning of the industrial revolution the burning of fossil fuels has

been emitting significant amounts of carbon dioxide (CO_2), which is now believed to be

affecting Earth's climate. John Tyndall began working with the heat-absorbing qualities

of gasses such as CO_2 in 1859 (Crutzen & Ramanathan, 2000). In 1896 Svante Arrhenius

projected that at some point anthropogenic CO_2 emissions might cause global warming

(Uppenbrink, 1996). In the early 1960s, Charles David Keeling was able to measure the

CO_2 level in the atmosphere and determined that it was steadily increasing (Quay, 2002).

While the scientific community had become aware of the potential for climate change,

little had been done to address the issue.

The Intergovernmental Panel on Climate Change (IPCC) stated in the Fourth

Assessment Report Executive Summary, published April 6, 2007, that as a result of

climate change, it is likely that the health of millions of people, especially the poor and

those with preexisting conditions, would be affected by decreased food security, extreme

weather events, and increased issues of diarrhoeal, cardio-respiratory and infectious

diseases. Now, even with application of the most stringent measures to reduce green

house gases (GHG), further climate change over the next few decades is inevitable

(IPCC, 2007).

As of July 22, 2007, a new Washington State Law becomes effective. In part, it

requires that all new thermal electric power plants to be built with integrated CO_2

separation equipment so that a defined amount of excess CO_2 production per unit of

power generated can be collected for "permanent geological injection" or permanent sequestration by "other approved means." So equipped, the units are designated as "capture ready." (Washington State Law, 2007) This law, intended to reduce GHG emissions, complements those of other states and hopefully precedes many more. While most of the laws in other states provide for a minimum amount of renewable energy that is to be produced by certain dates, Washington is looking to handle the emissions problem in no small way through "disposal" of the CO_2 generated by power plants.

The US federal government is moving along similar lines. For example, House of Representatives Bill 1933, introduced April 18,2007, is intended to amend the Energy Policy Act of 2005 "…to reauthorize and improve the carbon capture and storage research, development, and demonstration program of the Department of Energy, and for other purposes." (GovTrac, 2007/2008).

A number of methods for reducing CO_2 emissions are available, including cutting back on the amount of energy we consume, increasing the energy efficiency of industrial and personal activities, using renewable and nuclear energy as possible and storing/sequestering CO_2 produced by point sources, either geologically or through sequestration by mineral carbonation. This paper recognizes the contributions that each method can provide, but only investigates CO_2 storage/sequestration possibilities, comparing various methods of geological injection to a method of disposing of the CO_2 by converting it into an environmentally benign state through an additional chemical reaction.

THE PALEOCENE EOCENE THERMAL MAXIMUM

The Paleocene-Eocene thermal maximum (PETM) was a period in Earth's past demarcating the transition between the end of the Paleocene and the beginning of the Eocene Epoch. It occurred about 55 million years ago (Ma) and is typified by rising temperatures superimposed on a world that was already about $2^{o}C$ warmer than it is now (Bains et al., 2000). High atmospheric CO_2 concentration allows short-wave incoming solar energy to pass unhindered, but once the light energy has struck molecules of matter, such as the surface of the earth, it is absorbed and reradiated as long wave heat energy. High atmospheric concentrations of CO_2 trap the heat energy, and prevent it from being reradiated to space. This process is referred to as the "greenhouse effect."

The PETM greenhouse Earth condition occurred as a result of a large quantity of CO_2 of uncertain origin that had been released into the atmosphere and ocean. The carbon atoms in the CO_2 had a very low ratio of heavy ^{13}C stable carbon isotope atoms in relation to ^{12}C ($\delta^{13}C$). The low $\delta^{13}C$ occurred as a result of the CO_2 influx having been previously filtered by photosynthesis, which selectively accepts ^{12}C because of its slightly lower atomic weight and resulting slightly different chemical properties (O'Leary, 1988). As such it is generally accepted that high ^{12}C sedimentary methane hydrates, formed from decayed organic matter, situated interstitially within sediments at the ocean's floor along continental slopes, dissociated from their stable clathrate conformation en masse in response to an increased ocean-bottom heat increase of about $4^{o}C$. When the carbon dispersed into the ocean and atmosphere, it resulted in a reduction in ambient $\delta^{13}C$ (Kelly et al., 2005).

There is evidence that voluminous flood basalt magmatism, accompanying the opening of the North Atlantic Ocean, intruded carbon-rich sedimentary rocks that resulted in the production of metamorphic methane, which acted as a trigger for the massive release of methane hydrate carbon at the Paleocene-Eocene boundary (Storey et al., 2007). Methane hydrates appear to have been the source of the carbon for the CO_2 GHG that caused the 5^oC thermal increase. Anthropogenicly produced CO_2 may act as a trigger for our current inventory of methane hydrates.

The PETM manifest itself through global surface temperature increases of $5\text{-}7^oC$ over a period of about 30,000 years, producing a mean surface air temperature $6.7\text{-}8.5^oC$ warmer than today as a result of the elevated levels of atmospheric greenhouse gases. The heat persisted for about 60,000 years (Bains et al., 2000). The warming has been described as "intense" (Bains et al., 2000) and "particularly rapid" with "extreme magnitude" (Kelly et al., 2005). The PETM is an excellent, perhaps the best, analogy to our current increasingly warm climate resulting from atmospheric CO_2 (Pagani et al., 2006). Because of the quick warming over 30,000 years and the subsequent gradual return over a period of 100 to 200 thousand years (ky), the PETM event suggests that the climate system had been in disequilibrium (Kennett & Stott, 1991) and experienced negative feedback that reduced greenhouse gas concentration and buffered the ocean's acidity (Kelly et al., 2005). Earth's response to the global warming resulting from the rapid flux of atmospheric carbon in the lower Tertiary Period may be the best example in the geologic record of the Earth's negative feedback to high CO_2 (Bains et al., 2000).

Negative Feedback Resulted in Recovery from the PETM

As the ocean absorbed vast quantities of CO_2 during the PETM, it became more acidic. Dissolved CO_2 in the ocean reacts with carbonate ions (CO_3^-), to produce alkaline cations (Mg^+, Ca^+) and bicarbonate anions (HCO_3^-), buffering the ocean against the acidification. This reaction allows the diffusion of replacement CO_2 molecules into the ocean, while sacrificing the ocean's carbonate sediments. This effect represents the first stage of Earth's negative feedback mechanism against excess CO_2 levels (Kelly et al., 2005).

As a result of the high concentration of atmospheric CO_2, temperature and humidity during the PETM were also very high, resulting in a lot of rain that supported an abundance of land plants. High runoff rates would have carried the decayed organic matter resulting from plant decomposition to the ocean, and may have supported 60,000 years of sustained blooms of marine phytoplankton. The associated sequestration of excess CO_2 by marine phytoplankton, some of which sank to the bottom when the organisms died, caused the accumulation of carbon in the sediments (Bains et al., 2000). Abundance of kaolinite, a clay mineral, found in the stratigraphy at the PETM supports the idea that continental weathering and runoff were elevated at this time (Kelly et al., 2005).

A positive feedback system operated during the PETM that worked to maintain high atmospheric CO_2. Biochemical kinetics suggests that nearly all animals experience a doubled rate of basal metabolism in response to a $10^{\circ}C$ increase in temperature. As abyssal zone (2000-6000 meters deep) temperatures were about $10^{\circ}C$ higher than current day, expected organic-carbon burial was drastically reduced from what would be

expected because of the increased consumption required by the organisms for maintenance of basal metabolism (A. Olivarez Lyle & M.W. Lyle, 2006).

In addition to these feedbacks, the vast majority of permanent sequestration of CO_2 occurred as a result of accelerated weathering reactions of silicate rocks on land. The chemical reactions would have generated an influx of bicarbonate ions and various cations in solution into the ocean, further neutralizing the ocean's acidity and increasing the bicarbonate content until CO_2 equilibrated (Kelly et al., 2005; Zachos et al., 2005).

Silicate rock weathering on land follows the general formula:
$CaSiO_3 + 2CO_2 + H_2O \rightarrow 2HCO_3^- + Ca^{2+} + SiO_2$, and subsequent precipitation of calcite: $HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + CO_2 + H_2O$. Two CO_2 molecules are consumed during the silicate rock weathering, but only one is released during precipitation of calcite for a net uptake of one molecule. As a result of this reaction, the large amount of carbon dioxide generated during the PETM was permanently sequestered through weathering of silicate rock and precipitation of calcite in the form of limestone (Zachos et al., 2005).

A laboratory process for reacting CO_2 with solid minerals to produce other solid minerals has been in development since 1995. The process mimics Earth's CO_2 negative feedback through weathering of silicate minerals. In nature, high CO_2 levels in the atmosphere result in warm temperature, high humidity and a lot of rain containing significant carbonic acid. These conditions result in a very slow process of carbonate mineralization at a rate of about 100 million tons of carbon per year (Seifritz, 1990), which is less than 2% of global annual anthropogenic carbon emissions. Industrial

application of this process could provide CO_2 sequestration of nearly all of the CO_2 produced at any point source at a greatly accelerated rate, as a highly stable solid, for geologically significant time.

MINERAL CARBONATION, THE PROCESS

The method of chemically reacting CO_2 with another substance for the purpose of removing it from the atmosphere was first referenced by W. Seifritz of Switzerland in Science Magazine in 1990. He suggested that a chemical reaction between CO_2 and a common silicate mineral (feedstock) such as olivine ($Mg_2 SiO_4$) would react the carbon atom into a permanently stable, solid carbonate form, magnesite ($MgCO_3$), commonly found in nature (O'Connor et al., 2000).

The process is referred to as carbonation of silicate minerals. It is different than other CO_2 sequestration schemes in that it emulates Earth's own CO_2 negative feedback system that operated over a period of 10^5 years, reducing temperatures at the end of the PETM (Dickens et al., 1997; Kennett & Stott, 1991).

Various process methods of running the reaction have been tried. The most viable is referred to as the "aqueous process," where water is added to pulverized magnesium (Mg) or calcium (Ca) silicate mineral to form a slurry. Mg and/or Ca cations are extracted from the mineral as a result of mineral dissolution in the water, and react with CO_2 as it is bubbled through the slurry. This method results in the precipitation of the carbonate minerals, magnesite or calcite, plus silica gel (SiO_2) as end products (Lackner, Wendt, Butt, Joyce Jr. & Sharp, 1995).

The Reaction Occurs in Three Steps

First, the aqueous dissolution of the CO_2 produces carbonic acid, which in turn dissociates to a hydrogen ion (H^+) and bicarbonate ion (HCO_3^-) (aq).

$$CO_2 \text{ (g)} + H_2O \text{ (l)} \rightarrow H_2CO_3 \text{ (aq)} \rightarrow H^+ \text{ (aq)} + HCO_3^- \text{ (aq)}.$$
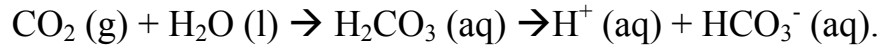
Second, the silicate mineral is hydrolyzed by the H^+ causing the magnesium ions (Mg^{2+}) or calcium ions (Ca^{2+}) to leach out of the rock and react with the HCO_3^-, forming a stable carbonate magnesite ($MgCO_3$) or calcite ($CaCO_3$), plus silica (SiO_2).

$$Mg_2SiO_4 \text{ (s)} + 4H^+ \text{ (aq)} \rightarrow 2Mg^{2+} \text{ (aq)} + SiO_2 \text{ (s)} + H_2O \text{ (l)}.$$

Third, the resulting carbonate mineral precipitates:

$$Mg^{2+} \text{ (aq)} + HCO_3^- \text{ (aq)} \rightarrow MgCO_3 \text{ (s)} + H^+ \text{ (aq)}.$$
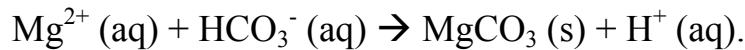
(O'Connor et al., 2001)

The key to harnessing the carbonation process for controlling fossil fuel CO_2 emissions is development of an economically competitive process that mimics natural weathering, but occurs at a greatly accelerated rate. The reaction occurs slowly at ambient and elevated temperatures when the pressure is below 7.4 MPa (73 atmospheres), which is the threshold for the supercritical phase of CO_2. Above 7.4 MPa at or above 31°C, the reaction rate increases significantly. Simply raising the temperature and pressure causes the reaction to occur even more quickly (O'Connor et al., 2000). There is an optimal temperature, which if exceeded, causes the chemical equilibrium to shift in favor of free CO_2 molecules. Inspection of the free energies of the reactants and

products allow computation of the highest temperature possible for the carbonation reaction, revealing the quickest and least expensive process application (Lackner et al., 1995).

The carbonation reaction occurs at the surface of the olivine crystal particles, coating them with carbonate and silica reaction products. The silica-rich "passivating layer" is thought to be rate-limiting. Observation of crystal surfaces during the progression of the carbonation process revealed that outside crystal corners routinely showed erosion, with intergrowth of olivine, silica and magnesite. It was clear that the erosion and intergrowth occurred during carbonation process, and is illustrative of the reaction progressing from the surface of the olivine crystal, inward. The layers are brittle, partially crystalline and partially amorphous. The layers are strained as a result of reorganization of the molecules. As such, the layers are subject to fracture and subsequent exfoliation. Adding some larger feedstock particles may promote abrasion at the surface of the particles, increasing the fresh surface available for reaction and reducing the cost of grinding. The resulting exposure of a fresh olivine surface enhances the reaction (Béarat et al., 2006).

Continuous stirring of the reactants in conjunction with good dispersion of supercritical CO_2 resulted in a 90% conversion within 24 hours (O'Connor et al., 2000). The rate of carbonate precipitation is dependent on the concentration of bicarbonate ion in the slurry. Experimental results indicate that the silicate dissolution rate is controlled by surface features, such as the amount of area presented for the reaction of the feedstock (O'Connor et al., 2001). In order to enhance passivating layer exfoliation, reactions are stirred causing collisions among the slurry particles, resulting in exfoliation of the silicate

surface features on the feedstock crystals (Béarat et al., 2006). Optimal particle size for a rapid reaction rate requires that some particles are less than 37 microns, though much of the material may be somewhat larger. The addition of abrasive particles such as quartz results in significant increase in the rate of carbonation rate increase. In addition, inclusion of larger feedstock particles may encourage the exfoliation due to abrasion. Albany Research Center has experimented with natural weathering, particle sizes and stirring the reactants in order to determine optimal conditions (O'Connor et al., 2001). Improvements are still being made to the process (Béarat et al., 2006).

Reactor Types

The original carbonation reactions were conducted in an autoclave or other high pressure vessel with a furnace, and a stirred-tank-reactor, in order to produce continuous heating and stirring. Records were kept of individual experimental parameters including pressure, temperature, particle size, rate of stirring, and use of additives (O'Connor et al., 2000).

Two types of full-sized reactors currently considered for sequestration plants are: the high temperature and pressure fluidized bed (batch-type), and the continuous pipeline reactor. The continuous pipeline reactor has provided results better than that provided by the autoclave system during small scale experiments. It is believed that mixing resulting from pipeline handling increases the particle-particle abrasion that is responsible for removing the silicate passivating layer and possibly the carbonated layer, exposing more reactive fresh surfaces (O'Connor et al., 2000; Béarat et al., 2006; Huijgen & Comans, 2005).

Source of Feedstock Mineral

Potential feedstock minerals are available as a result of large sections of ancient ocean floor that have been thrust onto certain continental margins as a result of continental-oceanic crustal plate collisions, which left portions of ocean floor at the surface of continental crust (Voormeij & Simandl, 2004). The western coast of North America and the eastern United States contain large amounts of this material. Over periods of millions of years, much of the original rock had been hydrated, creating the mineral serpentine, which is useful as feedstock, though the chemically bound water molecules must first be driven off by a costly heating process.

Enormous quantities of potential feedstock minerals are readily accessible (Lackner et al., 1995). An example of a possible feedstock mineral deposit is the Twin Sisters dunite massif, situated in northwest Washington State about 40 km east of Bellingham. The body is 16 km long, 5.5 km wide and about 2 km thick. The top of this unit is just over 2,000 meters elevation, placing the base of the structure near sea level. The body is composed entirely of dunite. As the northwest section is virtually unserpentinised, it could provide ideal feedstock for the process (Voormeij & Simandl, 2004).

METHODS OF GEOLOGIC SEQUESTRATION

In 2005 there were about 15,000 significant point sources of CO_2 worldwide. Approximately 8,000 of those were power plants. The balance included steel mills, chemical refineries, cement kilns and other industrial plants (Dooley et al., 2005). Just

over fifty percent of US electricity is generated by coal fired power plants (David, 2000).
As all of these plants are fixed in location and produce large amounts of CO_2, each
presents an opportunity to reduce emissions through capture and storage.

In order to store the CO_2, it must first be separated from the rest of the flue gases,
which are mainly nitrogen. A point source such as power plant must be equipped with a
CO_2 capture module, which may employ either a membrane or a chemical-reaction for
the separation process. Adding a capture system to an existing plant is complicated and
expensive, but can be more economically built into a new plant (MIT, 2007). Thus
equipped, a plant is designated as "capture ready." The nearly pure CO_2 stream is
compressed into a quasi-liquid referred to as its "super critical" state, and is pumped
through a pipeline to its storage or disposal site (Lackner et al., 1995).

There are several methods of carbon dioxide storage/sequestration that have been
described in the literature. CO_2 can be injected into the deep ocean; into oil and gas
reservoirs, regardless of whether the reservoir is depleted of hydrocarbons; into deep
saline aquifers; into unminable coal beds and flood basalt beds; absorbed by natural
sinks, such as forests; or through carbonation of silicate minerals as previously referenced
(Task Force, 2007).

In the deep-ocean-storage scenario, supercritical CO_2 would be bubbled into and
dissolved in the deep ocean water. Greater depth of injection provides a longer period
before the CO_2 is reintroduced into the atmosphere. Use of the ocean as a CO_2 repository
guarantees that storage will be temporary, as it will release much of the dissolved CO_2
when thermohaline circulation has brought the injected parcel of water back to the
surface. The method also has negative consequences for marine life. The increase in

dissolved CO_2 will lower the ocean pH as a result of the formation of carbonic acid, reducing the availability of carbonate ions necessary for the growth of organisms that build their shells out of calcium carbonate. As deep ocean ecosystems are not well understood, monitoring for unexpected consequences must be carried on (Caldeira, 2002). Currently the ocean turnover time is 800 to 1000 years, much too short a timeframe to be considered as long-term solution (Lackner, 2002).

The process of injection of supercritical CO_2 into partially depleted oil and gas formations can be is used to displace fossil fuel not retrieved through primary recovery from the reservoir via another borehole. This is referred to as secondary or enhanced oil recovery (EOR). The CO_2 used in this fashion can be left in the reservoir once secondary recovery has been completed. While this may be appropriate on a small scale for the purpose of increasing well production, it may not be appropriate for the wholesale storage of supercritical CO_2 because of the possibility of leakage.

As a result of the loss of certain structural support provided by the original fluid pressure, the previously nonpermeable reservoir walls and/or caprock may become cracked and incompetent to contain the CO_2. Any subsequent repressurization needs to be evaluated on a case by case basis (Task Force, 2007). As well, there are many unrecorded abandoned holes that have been bored into reservoirs and not soundly plugged. Early in US drilling history, there were no regulations requiring resealing of boreholes. Later, lack of proper materials and enforcement ensured that leakage from these formations is very likely (Massachusetts Institute of Technology [MIT], 2007). Major tectonic events such as thrust-fault earthquakes are expected to occur every few

hundred years in the Pacific Northwest, and could compromise the integrity of recharged structures leading to massive outgassing of CO_2 (Atwater et al., 2006).

Risk assessments are being developed with respect to various types of geologic-storage failure. Categories of risk include: features such as caprock thickness and reservoir permeability; events including well blow outs; seismic activity; accidental penetration of filled reservoirs by new wells; and processes including geochemical stress changes and chemical reactions within the chamber. Risk mitigation is based on careful site selection, monitoring, oversight and fixing problems that arise. Remediation for leakage is to attempt repair of the leak using oil and gas industry techniques. If that doesn't fix the problem, the CO_2 must be removed and put into a more competent reservoir (IPCC, 2005a).

A deep saline aquifer is a geologic formation that had been formed by original deposition of sand and or gravel. It is isolated from the sediments above and beneath it by an impervious cap and base; the pore-space is filled with saline ocean water. CO_2 can be pumped into such a structure, as has been done commercially since 1996. Located in the Norwegian North Sea, the Sleipner gas field is operated by Statoil, an integrated oil and gas company. Statoil separates most of the naturally occurring CO_2 from the natural gas that is extracted from a 3500-meter-deep formation. The CO_2 storage project has been run, in large part, to legitimately avoid paying Norwegian emissions tax (United States Department of Energy, 2007). Annually, Statoil injects roughly 1 million tonnes of compressed, supercritical CO_2 into the Utsira formation, a high-permeability, saline filled, unconsolidated sandstone unit that is about 250 meters thick and located at a depth of about 800 meters beneath the sea floor. The location of the injected CO_2 has been

followed through time-lapse seismic survey methods. As of 2005, the CO_2 bubble

covered about 5 km^2 (IPCC, 2005a), occupying the pore-space of about 1.25 km^3 of the

unit. Supercritical CO_2 has a density of about half that of water (Schrag, 2007), resulting

in a slight decrease to the force of gravity at that location. In 2002, a microgravity-

change survey baseline was established. Repeat surveys will provide high accuracy time-

lapse data (Zumberge & Eiken, 2003).

Enhanced coal bed methane technology is in an early development stage (Task

Force, 2007), as is the use of flood basalt formations for sequestration. If the flood basalt

sequestration process is subsequently shown to be viable, the United States and India

would have such geologic storage available (McGrail et al., 2006). Forest sequestration

has a limited capacity and a lifetime of only a few hundred years because the trees will

die and the sequestered carbon will then be reemitted to the atmosphere as the wood

decays.

COST OF GEOLOGIC VERSES MINERAL CARBONATION SEQUESTRATION

Capital cost of capture equipment is a major factor for any type of

storage/sequestration because CO_2 must be first separated from the exhaust stream of the

point source emitter. The new Washington State Law mentioned earlier requires in part

that any new power plant built in the state for electricity generation must be capture ready

(Washington State Laws, 2007). Once a plant has been equipped with a separator, the

capital cost of the equipment can be ignored in absolute cost comparisons between

methods of emission avoidance practiced at that plant.

Cost of operating the capture equipment only accrues when it is actually being used to separate CO_2 from the rest of the flue gas. The cost of capture includes compression of the CO_2 into a supercritical state. Using an Integrated Gasification Combined Cycle (IGCC) power plant to compare the cost of operation of the entire plant both with and without separation, the cost of capture has been determined to be about $15/tonne, at 85% capture efficiency (Table 1; Gielen, 2003).

Cost of transporting the CO_2 is relatively inexpensive by pipeline, or by ship if over long distances. By pipeline, cost may range from $1 to $10/tonne. Actual cost would vary as a result of difference in transportation distance and volume (Gielen, 2003). Making an assumption that CO_2 would need to be piped a similar distance to either a carbonation plant or to a geologic repository; the same cost of shipping a tonne can be applied. I'll use $5/tonne for comparison (Table 1).

Cost of mining, crushing and milling of ore is estimated at $8/tonne based on mining activity in other industries (Lackner et al., 1998). That value is used in Table 1.

TABLE 1. Cost of CO_2 per tonne avoided

	Geologic	Carbonation	
Capital cost capture equipment	fixed	fixed	
Cost of operating capture eqpt	15	$15	(Gielen, 2003).
Cost of transportation	5	5	(Gielen, 2003)
Mining and milling	n/a	7	(Lackner, 1998)
Cost of the mineralization	n/a	54	(O'Conner, 2004a)
Cost of geologic sequestration	5	n/a	(IPCC, 2005a)
Cost of mitigating leakage	unknown	0	
Ancillary income	unknown	unknown	
Subtotal	25	81	
Factor	x1.0	x1.3	(sequestered to avoided)
Total	$25	$105	

Cost of the baseline mineral carbonation process using dunite, the most favorable feedstock mineral, is approximately \$54/tonne for CO_2 sequestered and \$78/tonne for CO_2 avoided (O'Connor et al., 2004). A tonne of CO_2 "avoided" includes a tonne of CO_2 produced by the power plant during power generation for the grid plus another .3 tonne CO_2 created as a result of operating the carbonation process. I'll assume that the first plants deployed will be near the most favorable bodies of minerals such that the carbonation cost will be \$54/tonne disposed (Table 1).

Studies of the cost of using depleted gas or oil wells, or deep saline aquifers for storage produce widely disparate figures ranging from \$0.20 to \$30/tonne of CO_2 stored. A large Australian data set indicates that available onshore storage sites would average about \$5/tonne (Table 1; IPCC, 2005a). Cost of monitoring filled geologic formations is estimated to be about 3¢/tonne. This small amount is excluded from Table 1. Cost of mitigating leakage is potentially enormous though unknown (IPCC, 2005a), as such; it is excluded from Table 1.

Potential ancillary income as a result of mineral carbonation feedstock mining and processing may result through the recovery of other minerals such as iron, manganese, copper chromium, nickel and cobalt (Voormeij & Simandl, 2004), with an early estimate of \$10/tonne of CO_2 disposed (Lackner et al., 1998). In the case of geologic storage with EOR application, there could be revenues in excess of the cost of acquiring the reservoir and handling the CO_2 (IPCC, 2005a). Cost of remediation of leaking storage has not been estimated (IPCC, 2005a). As there are no reasonable estimates that can be used for either storage or sequestration method, neither potential cost reduction nor contingent remediation expense for either route is considered in Table 1.

ENVIRONMENTAL IMPACT

Environmental impact is inevitable for virtually any large-scale activity associated with sequestration or carbonation. In the case of ocean storage, CO_2 is injected into the marine environment. The deepest injection, at 3000 meters, provides the longest-lasting storage. After 1,000 years, 40% of the injected CO_2 would have reentered the atmosphere (Caldeira, 2002). Because this disposal results in a lowering of ocean pH and the eventual rerelease of CO_2 to the atmosphere, this method is simply not a viable option.

Geologists and engineers have a poor understanding of how abandoned wells will behave over long periods of time (IPCC, 2005a). Significant leakage is a distinct possibility. Many natural reservoirs of oil and gas have held pressurized deposits for millions of years, but there are empty reservoirs that obviously held oil or gas in the past, which has leaked out. There are reservoirs that currently leak without human intervention. As the formations best suited for storage have maintained their competency until their contents were removed, it would appear that they would best serve to store CO_2. This is not necessarily the case. During exploration and extraction, holes are drilled through the caprock. As contents are withdrawn, pressure is reduced, thus the chamber may settle, as evidenced by sinking of the ground above a depressurized gas structure. Settling may cause the caprock to crack. Subsequent repressurization with CO_2 may cause the reservoir to start leaking, not necessarily right away or even in the immediate vicinity of the bore hole (Gielen, 2003). Potential reservoirs may have existing wells that penetrate the caprock (MIT, 2007). Even a small rate of leakage

would produce a significant effect, like a dripping water faucet, and as there are no data on leakage rates for underground reservoirs, estimates are highly variable. Thus, the storage site must be monitored indefinitely.

Saline aquifers are common throughout the world, offering potentially large volumes of storage. Because of the lack of any existing database, such as exists for gas and oil reservoirs, saline aquifers have not been well-characterized (Voormeij & Simandl, 2003).

It is important to recognize the potential for ecological damage that could result at Earth's surface pursuant to storage/sequestration activity. The possibility exists for both geologic and mineral carbonation methods. The difference in overall impact lies in the likelihood of CO_2 leakage into the atmosphere from geologic repositories, compared to localized ecosystem damage resulting from operation of both the fossil fuel and feedstock mines in the case of mineral carbonation.

When fossil fuel hydrocarbon molecules are oxidized through combustion to release energy they produce CO_2 as a waste product. It is not necessary that the CO_2 produced by combusting fossil fuel be released to the atmosphere, rather the carbon can be further chemically reacted to move it into a stable state as a mineral carbonate (Lackner et al., 1998). Mineral carbonation provides a solution to the CO_2 emission issue without the potential for even accidental release; the process itself does not generate harmful by-products (Voormeij & Simandl, 2003). Through mineral carbonation, the carbon atom in the CO_2 is further oxidized, releasing about 1.5 kilojoules of heat energy per tonne of CO_2 released (Zevenhoven, 2004). The more highly oxidized carbon atom

cannot revert to CO_2 without the addition of heat. It is therefore chemically very stable and has little environmental impact (Lackner et al., 1998).

LOCATING THE CARBONATION REACTION SITE

In order to process a tonne of CO_2, it would take 2.3 to 3 tonnes of feedstock mineral (Voormeij & Simandl, 2003). Because of the high cost of transportation, the liquid and less massive CO_2 would be moved to the carbonation site for reaction. Processing will be done at the mineral mine site and the resulting solid reaction products would be stored in place of the removed feedstock mineral (Lackner et al., 1995).

Alteration of the ecosystem will occur only at the surface of the feedstock mineral mine site. The mineral would be removed from the mine, processed and the resulting carbonate returned to the void. As a result of mining activity, the overburden, or other material removed and subsequently returned to the excavation site becomes more voluminous. Change to the surface profile at the feedstock mine will occur as a result of this so-called "swell factor."   Mining regulation CFR §816.105 (b) (3) requires application of the concept of "approximate original contour" such that replacement of the "gangue," or spoil materials follows the original land configuration as closely as possible. Use of vegetation cover and construction of windbreaks should provide adequate control of potential soil erosion or landslides at the site, which should comprise the major potential environmental impacts (IPCC, 2005c). Since mineral carbonation requires mining activity and attendant surface disruption at both the feedstock mineral mine and the coal mine, and assuming similar impacts at each mining activity, roughly twice the costs (both monetary and environmental) would result.

DISCUSSION

Taking Earth's Lead on CO2 Sequestration

Atmospheric CO_2 concentrations have been high on Earth before, for example during the PETM. In response, Earth operated its own negative feedback system to restore equilibrium. This should provide a valuable example as to whether mineral carbonation verses geologic storage ought to be deployed as the principal method of reducing CO_2 emissions.

Feedstock Mineral Availability

Potentially useable feedstock minerals are vastly more available than all the fossil fuel on Earth and are to be found in easily accessible sites (Lackner et al., 1995). If serpentine is also found to operate well under industrial conditions, there will be no shortage of feedstock minerals in British Columbia and along the US coasts; however, if only magnesium olivine (forsterite) is found to be acceptable for the process, supplies of potential minerals would be both limited and available in only a few areas (Voormeij & Simandl, 2003). Based on the work done so far, it is likely that if olivine is found to operate well on an industrial scale, serpentine would also work, though it would be more expensive because of the extra energy required to activate it. The best feedstock mine site in the Pacific Northwest is Twin Sisters dunite, located 40 miles east of Bellingham, Washington.

Comparison of Methods for CO₂ Storage

Pumping CO_2 into the ocean is not a viable option due to the short residence time until it is re-emitted. The public appears to consider use of the ocean as a CO_2 repository to be the least acceptable method (Voormeij & Simandl, 2003). Pumping supercritical CO_2 into geologic formations is also not a good idea because of its potential mobility and because of the difficulty of remediation if a problem is detected.

Use of saline aquifers opens large volume for storage of CO_2, but concern for safety and potential leakage may significantly reduce availability. As CO_2 is injected, reservoir pressure would immediately begin to rise, which could lead to fissure widening and seismic activity providing leakage pathways (Lackner, 2002). As the CO_2 underground is buoyant, it would tend to rise to the surface upon escape from immediate containment. Concerns over safety and leakage would substantially limit the amount of storage these aquifers might provide (Lackner, 2002). Site-specific data are necessary in order to accurately evaluate the competence of a particular saline aquifer, and only those units that have undergone detailed evaluation could be considered for actual storage. Once a number of aquifers have been evaluated, general guidelines could be developed (Task Force, 2007), but so far there are only limited data on specific potential reservoirs.

While Statoil is monitoring its Sleipner project for leakage with seismic and micro-gravity time series surveys (Zumberge & Eiken, 2003), the company won't be able to detect loss until it actually happens. Leakage could occur if the CO_2 bubble reached a major breach in the saline formation's caprock. It may not be possible to remediate such a high volume reservoir 800 meters beneath the sea floor. Research is continuing as to whether deep saline aquifers should properly be considered permanent over geologic time

or merely temporary storage (McKelvy et al. 2002). Continuous monitoring is necessary because of this lack of certainty.

Although years of experience with CO_2 injection for enhanced oil recovery projects have accumulated, little data about leakage have been collected. Leakage rates might rise as reservoirs fill. If several millennia pass before substantial leakage of the geologically stored CO_2 occurs, Earth's carbon cycle will have time to redistribute it among natural systems (Schrag, 2007). Alternately, if all Earth's hydrocarbons were oxidized and the CO_2 stored geologically, the secure storage lifetime would need to be many thousands or even many tens of thousands of years (Lackner, 2002).

It is unknown whether any geologic reservoirs are competent to contain stored CO_2 without leaking over periods of tens of thousands of years. The manager of Statoil's Saline Aquifer Carbon Dioxide Storage Project states that the storage is highly unlikely to leak for the next several hundred years, and that staying there for the next 5,000-10,000 years "must be good enough" (Statoil, 2004). Computing the amount of carbon that will result from combustion of our remaining 200 years worth the coal world wide (United States Department of Energy [DOE], 2004), at our current rate of emission of 6 gigatonnes (Gt) carbon/year from combustion of fossil fuels (David, 2000), provides a figure of 1,200 Gt carbon produced. Assume that all of it is stored geologically and leaks out during the following 10,000 years. That occurrence would constitute a carbon release of a similar amount, over a similar period of time, as the approximately 1,500 Gt of methane carbon that had generated the PETM (Storey et al., 2007; Dickens et al, 1997). While the PETM endured for a period of 30,000 years, the amount of time that the CO_2 remained in the environment, the onset or $\delta^{13}C$ excursion segment lasted between

approximately 6,000 years (Kennett & Stott, 1991; Kelly et al., 2005) to 10,000 years (Dickens et al., 1997). Using Statoil's most conservative estimate of storage life, significant leakage could conceivably generate a new atmospheric thermal spike similar to the PETM.

Because of this wide range in predictions for the rate of leakage from geologic storage sites, the validity of this option for storage of CO_2 is uncertain. In order to solve our emissions problem in part through storage, we need to remove the CO_2 permanently rather than just temporarily storing it. Pumping it into a reservoir with the hope that it will stay there long enough that sufficient atmospheric dilution will occur as it leaks out does not constitute adequate planning. It is irresponsible to deal with a major problem such as high atmospheric CO_2 concentration by setting up another in its place because it is cheaper or easier than fixing the problem. More completely oxidizing the carbon to its carbonate form is arguably the best way to handle our CO_2 problem. Mineral carbonation sequesters CO_2 on a geologic timescale with virtually no chance of release at a later time (Voormeij & Simandl, 2003). It is virtually certain that after a millennium, 100% of the carbon sequestered through mineral carbonation will remain in place (IPCC, 2005c).

The Cost of Mineral Carbonation is Greater than Geologic Storage

The new Washington State Law requires in part that new thermal electric power plants be equipped to store a certain excess amount of the CO_2 produced. While it will take decades for new plants so equipped to replace the present plants, the future will include CO_2 storage/sequestration. The decision to store CO_2 in geologic repositories or

through mineral carbonation will be largely decided by whether the low cost of the geologic storage option or the certainty of mineral carbonation prevails.

Using the estimates provided in Table 1, evaluation of the relative cost of geologic storage verses mineral carbonation provides a total cost of geologic storage of $25 per tonne of CO_2 disposed, plus unknown potential liability if leakage occurs. The total cost of mineral carbonation is estimated at $105 per tonne of CO_2 avoided with no lingering unknowns. These figures translate roughly into an additional cost of electricity (COE) of 2.5 ¢ per kilowatt hour (kwh) for geologic storage and 10.5¢/kwh for mineral carbonation, based on an estimated additional 1¢ per kwh electricity per each $10/tonne of CO_2 stored or sequestered.

The average residential COE in January 2007 over the entire United States was 10.05¢/kwh. Idaho enjoys the cheapest rate at 5.69¢/kwh; Hawaii has the most expensive at 21.77¢/kwh. Industrial, commercial and agricultural rates are somewhat lower for each state (Energy Information Administration, 2007). Adding 10.5¢/kwh for mineral carbonation would double the COE overall. This amount would pay for the entire program of running mineral carbonation for all power plants in the USA.

The new Washington State Law explicitly provides that the costs associated with emissions reductions will be internalized by the electric utilities (Washington State Laws, 2007). Ultimately the cost will be paid by the consumers. The COE increase would occur over a period of decades as old, inefficient power plants are replaced with efficient, capture-ready plants with carbonation equipment. The additional COE would seem to be manageable by consumers without serious disruption to the economy. Certain relief against the additional cost would be provided by the stimulation of the economy that may

be expected as a result of developing a clean power system. Over just the last few years the cost of gasoline in the US has tripled, but the economy has not been crippled by the increase.

In our current market economy, supply and demand determines price. The practice eschews lives forfeited and health forgone as a result of ignoring externalities. As mortality and morbidity are not directly convertible to a dollar amount, an appropriate dollar value cannot readily be fixed for them. A working estimation of the externalized cost of a tonne of CO_2 emitted has been suggested by the IPCC Working Group II through evaluation of peer-reviewed estimates for 2005. The values range from $3 to $130/ tonne with a mean of $12/tonne (IPCC, 2007). If this figure is accurate, it would appear unwarranted to even spend the money on geologic sequestration at $25/tonne. It would be informative to see whether and how the cost of deaths, health, hurricane activity, sea-level rise and destruction of ecosystems has been handled in arriving at the estimate. In addition, the cost of geologic storage only includes acquisition of the right to use a particular reservoir for disposal and the preparation and transportation of the CO_2; it does not include any assumed liability for the leakage that may ultimately occur. Legal issues, such as who owns the disposed-of CO_2 and what remedies, both mechanical and financial, should be pursued in case of loss of integrity of the structure need to be resolved. Permanent liability may be assumed against the owner (Herzog, Caldeira & Reilly, 2003). A funded insurance mechanism backed by a government guarantee would need to be implemented in order to handle the possibility of catastrophic and/or long-term storage failure (MIT, 2007). While the cost of such potential problems must be added to the $25/tonne cost of storage for geologic formations to arrive at a more realistic figure

for comparison to mineral carbonation, the appropriate dollar amount is unknown (IPCC, 2005a).

The cost of mineral carbonation in excess of geologic storage may provide commensurate benefits by alleviating the uncertainty of temporary storage. At the crux of this debate, paying for the externalities of emissions generated, along with the electrical power by the electric utilities, and ultimately the consumers, is appropriate and should have been considered long ago. As mineral carbonation does not suffer the drawback of leakage that is possible with geologic storage, the cost disparity between the methods is not as large as it appears based on comparing the figures in Table 1, but the difference in the level of potential ecological damage is enormous.

Our society desires to provide health care for everyone because it is a social rather than an individual issue. Reduction of communicable disease benefits everyone even though the cost is not equally borne. In the case of CO_2 storage, most of the cost to us and to future generations will be paid as we go via our power bills, regardless of the storage method used. Public funds, taxes and subsidies will assist in handling the transition. The financial cost of doing it right can be managed.

Relative Environmental Impacts of Geologic Storage and Mineral Carbonation

The risks associated with long-term underground storage are not well understood. Use of geologic reservoirs is considered to be temporary storage due to the paucity of knowledge regarding the potential for both gradual leakage and accidental release over long periods of time (IPCC, 2005b). Risk factors include above-ground issues such as pipeline failure and well-head leakage. Experience in oil and gas industries provides

certain expertise useful in making a reasonable determination of such risk and in setting up contingency plans for handling potential CO_2 spill situations. Risks associated with long-term underground storage itself, however, are not well constrained. Experience gained during decades of large-scale underground storage of natural gas and in storage of hazardous nuclear waste can provide some direction in managing underground storage, but our knowledge of the behavior of repressurized reservoirs over periods of hundreds or thousands of years is nonexistent. Risk assessment studies are under way to provide guidelines on how to handle problems that may occur (IPCC, 2005a).

For mineral carbonation, negative environmental impact is limited to the location of the CO_2 pipeline and to the mining sites of both the feedstock minerals and the coal. As the reaction products are not water-soluble, they will not be spread beyond the immediate area of containment. Mining the feedstock and storing the reaction products produces a relatively significant environmental impact to a small area rather than diluting it over a large area (Lackner, 2002).

The ecological impact of the pipeline for both geologic storage and mineral carbonation sequestration would be comparable, assuming similar shipping distances. This leaves a comparison of the potential for leakage of geologic storage over the next several thousand years against the disruption at the surface ecosystem from mineral carbonation activity. The difference is significant and it can be argued that mineral carbonation is superior with respect to environmental issues when compared to geologic storage.

Industrial Sized Application of Mineral Carbonation Process

Although the mineral carbonation method is not currently cost competitive with temporary geologic storage, it is important to investigate the potential of full-scale industrial application because of the permanence and stability of the reaction products. Earth operated the method on much grander scale, but we must increase the reaction rate by orders of magnitude over that which occurred during the PETM.

Klaus Lackner began working with the mineral carbonation process in 1995 supported by Department of Energy funding. Experimentation by numerous workers over the last 12 years has shown that the process has no insurmountable obstacles. Research under industrial conditions is a next step (Huijgen & Comans, 2005). Until such trials are run, it will not be known whether the process functions well at large scale and rapid rate. Following through with industrial deployment will present the opportunity to define relevant issues and obtain operational experience, which could reduce investment and operating costs (Gielen, 2003). Geologic storage has much less cost-reduction potential.

While we didn't suspect that emitting CO_2 would cause a problem until a few decades ago, we do know there could be significant problems with geologic storage. We don't know how soon or how bad it will be or whether we'll even be equipped to handle them. Use of geologic storage is a recognized gamble by the current population without knowing the odds against failure; it trades our CO_2 concentration liability for some future CO_2 concentration liability.

PLAN FOR ACTION

The new Washington State Law Chapter 307, Laws of 2007, "Mitigating the Impacts of Climate Change" was signed by the governor on 4 May 2007 and becomes effective 22 July 2007. The law states in part that the act is meant to authorize immediate action against GHG resulting from the generation of electric power. The law provides a timetable for reducing overall GHG emissions in the state to the 1990 level by 2020, to 75% of the 1990 level by 2035 and to 50% of the 1990 level by 2050. In addition, the governor is to develop policy recommendations to the legislature regarding a process for replacement of the highest GHG-emitting plants that have exceeded their expected useful life. The law provides that as of July 1, 2008 the GHG "emissions performance standard" of any new thermal-electric plant shall be 0.5 tonne CO_2 emissions per megawatt-hour, roughly half the current amount, requiring any new Washington plant to be capture ready. The resulting captured CO_2 is expected to be injected into geological formations or sequestered by other means, which could include mineral carbonation. The new law states that such activity is expected to spur technology, increase plant efficiency and result in an economic boost for the state (Washington State Law, 2007). As a result of the application of the new state law, it is clear that CO_2 storage is in Washington's immediate future.

If an accident during early deployment of geologic sequestration occurs, or if there is strong opposition by grassroots organizations, continued use of geologic sequestration could be as difficult to implement as radioactive waste repositories (Wellington et al., 2007).

CONCLUSION

Atmospheric CO_2 concentrations have been high on Earth before, for example,

during the PETM. In response, Earth operated its own negative feedback systems,

bringing the level back to equilibrium (Bains et al., 2000; Kelly et al., 2005). Mineral

carbonation mimics Earth's system for restoring the balance of CO_2 in the environment

through permanent removal of the excess CO_2.

CO_2 storage is in its infancy; experience, organization and methodology must be

further developed (Task Force, 2007). The most obvious method of disposal is to pump

the CO_2 into geologic reservoirs, especially if there is oil or gas that could not be

removed by pumping. The most obvious method, however, is not necessarily a good

solution.

Federal governments around the world; several states including Washington;

voters of the City of Boulder, Colorado; The Evergreen State College; and individuals

who choose to pay for green power from their utility companies are among those who are

working to ameliorate climate issues, while eschewing immediate financial cost as the

one and only consideration. Their perspective of the relative importance of the climate

versus the lowest dollar amount that could be paid supports the contention that if mineral

carbonation is superior to storage of CO_2 in geologic formations, we must provide

appropriate consideration in further developing the method, regardless of the resulting

increase of COE.

The new Washington State Law specifically addresses the environmental

externalities of CO_2 emissions. It also requires that all new coal-fired power plants

coming on line be CO_2 capture ready. Application of the same type of forward reasoning

to mineral carbonation would provide support for development and deployment of the mineral carbonation process.

In order to determine whether mineral carbonation will operate on an industrial scale, a suitably sized plant must be built. If it works, we could continue to use coal for our energy needs; it would become almost environmentally friendly. The learning curve will have started; the process will become cheaper sooner. We will have had a head start with regard to regaining Earth's CO_2 balance. Our remaining coal deposits have been estimated to be enough for the next 250 years at our current rate of use (United States Senate Committee, 2006). Hopefully by the time we've exhausted our supply, we'll have invented and deployed alternative energy-production methods.

If mineral carbonation is shown to work, it should be deployed prior to having filled geological repositories to the point where the situation could be dangerous. There's a difference between preparing for a thrust-fault earthquake that could happen tomorrow, and the blow-out of CO_2 reservoirs that shouldn't have been filled in the first place. Accidents don't happen, they're orchestrated. If we move with mineral carbonation as soon as possible, regardless of price, we'll have an opportunity to fix the GHG problem. If the mineral carbonation process doesn't hold up to full-scale application, it would be either abandoned or studied further, in which case we'll need to phase out the use of hydrocarbons all together. This will be difficult, perhaps not even possible, while maintaining our civilization.

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