Carbon Sequestration via Mineral Carbonation: Overview and Assessment

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Overview

This report is being written for the Carbon Sequestration Initiative at the request of two members, GM and ChevronTexaco. The purpose is to give a brief overview and assessment of carbon sequestration by mineral carbonation (referred to as "mineral sequestration" in this report). The assessment is to highlight areas that need development in order for this technology to become commercial, not to do an in-depth, independent analysis of the technology. To accomplish this goal, I reviewed some current articles from the literature and talked to several of the key researchers involved. The resulting draft was then reviewed by one of the technology's proponents.

ZECA (Zero Emission Coal Alliance) combines a capture process with mineral sequestration. However, this report looks only at sequestration, not capture, because it is possible to use mineral sequestration with a wide range of capture processes. Therefore, reviewing the ZECA capture process is beyond the scope of this report.

Mineral sequestration was first mentioned by Seifritz (1990) and discussed further by Dumsmore (1992). However, Lackner *et al.* (1995) were the first to provide the details and foundation for today's research efforts. The first significant research program on mineral sequestration was at Los Alamos National Laboratory (LANL) under the direction of Klaus Lackner. To continue this work, a team of researchers from LANL, National Energy Technology Laboratory (NETL), the Albany Research Center, and Arizona State University was formed in 1998 under the sponsorship of the US Department of Energy. Much of the information presented in this report is a result of their work.

This main body of this report is divided into three sections, followed by a short conclusion. The sections are:

- Motivation and Scientific Basis
- Reaction Pathways
- Assessment

The first two sections summarize the literature without editorial comments. The assessment section highlights the identified areas for R&D and puts the proponents claims in perspective.

Motivation and Scientific Basis

There are three advantages that are generally given to motivate the need for mineral sequestration R&D. The first is that carbonates have a lower energy state than CO_2. Therefore, at least theoretically, the process not only requires no energy inputs, but also can actually produce energy. The free energy of several key carbon containing compounds are shown in Appendix 1. A more detailed explanation from Yegulalp *et al*. (2000) follows:

> The carbonation reaction can be shown by the simple reaction of binary oxides, MgO and CaO. These reactions are exothermic.
>
> $$CaO + CO_2 = CaCO_3 + 179 \text{ kJ/mole}$$
>
> $$MgO + CO_2 = MgCO_3 + 118 \text{ kJ/mole}$$
>
> Even compared to the heat released in the combustion of carbon (394 kJ/mole), these reactions release substantial heat. In nature, however, calcium and magnesium are rarely available as binary oxides. They are found typically as calcium and magnesium silicates. The carbonation reaction is still exothermic for common calcium and magnesium bearing minerals. In such cases however, the heat release is reduced. As an example consider the carbonation reactions of forsterite and serpentine. For forsterite and serpentine respectively:
>
> $$\tfrac{1}{2}Mg_2SiO_4 + CO_2 = MgCO_3 + \tfrac{1}{2}SiO_2 + 95\text{kJ/mole}$$
>
> $$1/3Mg_3Si_2O_5(OH)_4 + CO_2 = MgCO_3 + 2/3SiO_2 + 2/3H_2O + 64\text{kJ/mole}$$
>
> Both of these reactions are favored at low temperatures. In nature magnesite and silica are common in serpentinized ultramafic rocks. Their formation is due to natural CO_2–rich fluids percolating through mineral deposits. Magnesite is stable and not likely to release the bound CO_2 again.

The second advantage is that the raw materials are abundant. Once again from Yegulalp *et al*. (2000):

> Calcium and magnesium carbonates are solid which is desirable in above ground disposal. The materials formed can be stored at the serpentine mine as landfill and will not leave the disposal site. Magnesium proved more attractive since there are large deposits of magnesium rich minerals. Peridotite, and serpentinized peridotite rocks can have an MgO content between 35% and 40% by weight, whereas abundant calcium silicates rarely have more than 12 % to 15% of CaO by weight. In addition, the magnesium silicates are more reactive and are therefore more suitable for above ground carbonation.
>
> The process implies a large mining effort, but the areal extent of the mine is small compared to the coal mine that produces an equivalent amount of coal. Overburden on serpentinite rock is generally insignificantly small and the minerals occur in thick layers rather than thin seams. Nevertheless, the mass of material required is larger by a factor of six than the mass of coal that is used as fuel. As a result, the formation of carbonate will have to be performed at the mine site, and the resulting silica and carbonates will be stored in the mine. Since volumes increase in the process, some modification of the local terrain's profile is unavoidable.

> Mining costs appear to be quite low. The mining is similar to copper mining and the amount of peridotite required for a GW power plant is small compared to the amount of ore mined in a large copper mine. Cost estimates, based on other mining operations suggest a cost of about $8 per ton of CO_2.

The final advantage is that this is the only form of carbon sequestration that is "permanent". The other major proposed sequestration options -- terrestrial (soil and trees), geologic, and ocean – have the potential for leakage over time. Leakage can make the sequestration ineffective if the CO_2 returns too quickly to the atmosphere. In addition, leaks may present other environmental, health, or safety issues. Mineral sequestration has none of these concerns.

Reaction Pathways

The key technical challenge for mineral sequestration is how to react the naturally occurring minerals to carbonates. While the reaction is thermodynamically favored, it is extremely slow in nature (characteristic time on the order of a hundred thousand years). The challenge is to speed up the reaction in order to be able to design an economically viable process. There are many potential starting materials and reaction routes for mineral sequestration. Highlighted below are the primary reaction pathways that have been or are being investigated.

As explained in the previous section, attention has focused on Mg-containing minerals (vs. Ca) because they are more concentrated (35-40% MgO vs. 12-15% CaO by weight) and more reactive. Furthermore, research has focused on using serpentine ($Mg_3Si_2O_5(OH)_4$) as the starting material because it is much more abundant and accessible than the olivine (Mg_2SiO_4).

The simplest process would be direct carbonation – reacting the rock directly with the CO_2. However, the kinetics of this approach are much too slow. Much faster kinetics can be obtained by first dissolving the minerals in solution. Here the key is how to effectively dissolve the rock.

Initially, HCl was used to dissolve the minerals. Serpentine readily dissolves in an HCl solution. Then, water needs to be driven off in order to precipitate out the $Mg(OH)_2$, which can then be readily reacted with CO_2. However, this process is too energy intensive because of the large number of steps and the need to drive off a significant amount of water.

To get around the problem of removing large quantities of water, the serpentine can be dissolved in molten $MgCl_2$ salts. Then CO_2 can be added to this solution to produce $MgCO_3$ and the molten $MgCl_2$ salts can be recycled. However, there are many operational difficulties due to the highly corrosive nature of this process.

Most of the recent effort has focused on dissolving the serpentine in aqueous solutions without having to use acid. A major challenge here is how to get the serpentine to dissolve in the water in a reasonable amount of time. At the Albany Research Center, they have made great strides using a pre-treatment. However, this pre-treatment is very energy intensive, requiring 200 kWh per ton of serpentine (a 20% energy penalty for a coal-fired power plant). Alternatively, the serpentine can be ground, but the energy for this may be as great as the pre-treatment. To help dissolve the serpentine, it was found that adding Na_2CO_3 to the solution was beneficial. Initially, this process required high pressures to operate at (150 atm), but that requirement has recently been lowered (30 atm). Finally, the $MgCO_3$ is separated via precipitation, but since it is such a fine precipitate, dewatering has been a problem.

In addition to the pathways outlined above, other methods have also been tried. While there has been progress, none of the pathways has yet demonstrated that it can be the basis of a commercial process. For example, the work at the Albany Research Center still needs to improve or replace the pre-treatment step and to address the dewatering problems to be in a position to start scale-up. Alternatively, some have suggested using this process starting with olivine. Olivine dissolves much more readily, so pre-treatment may not be necessary. However, olivine is not nearly as abundant as serpentine by about an order of magnitude. Another suggestion has been to go back to using acid to dissolve the minerals, but use a milder acid (e.g., acetic acid) as opposed to HCl.

In summary, many reaction pathways have been explored to vary degrees. While progress is being made, none has resolved all the issues necessary to make a commercial process. However, there is no lack of ideas on potential ways to scale the barriers.

Assessment

This assessment analyzes mineral sequestration processes from the viewpoint of the three key features that proponents most often cite as motivation to invest in these technologies. These are favorable thermodynamics, abundant raw materials, and permanence of the storage. In addition, a section is included on costs.

Thermodynamics and Kinetics

The fact that carbonation reactions are thermodynamically favored is a positive attribute, but by itself is not sufficient proof of a practical process. It only tells us that a practical process is not impossible. The challenge of overcoming very slow reaction kinetics must still be addressed. This is the single most critical challenge for mineral sequestration.

While the understanding of the potential reaction pathways has improved significantly based on research to date, there is still a long way to go in developing a cost-effective route for mineral sequestration. One must be cautious when about reading too much into results like “78% conversion in 30 minutes” (O’Connor *et al*., 2001). These rates were obtained by first pre-treating, which improved the kinetics at the expense of significantly increasing the energy requirements. Processes must have *both* acceptable kinetics and acceptable energy needs.

Research to develop viable reaction pathways is still in an early stage and there are many potential solutions that need to be investigated. On the other hand, there is no guarantee of success, i.e., finding a fast enough reaction pathway that is commercially acceptable (in terms of cost, energy use, and other issues like corrosion and dewatering). Only through more research will we better understand the potential for success.

Raw Materials

The large amount of materials required for mineral carbonation is an important issue that needs to be addressed. Based on reasonable assumptions from Goldberg *et al.* (2001), the mass of magnesium silicate ore required to store the carbon generated by coal combustion is over eight times the mass of the coal (see calculation in Appendix 2). It is claimed that despite the large differences in mass, that the mining operation for the serpentines would be similar in scale to the coal mining operations because the overburden is small and the serpentines exist in thick layers. In reality, while this may be a true generalization, there would exist a range of conditions (in terms of overburden, thickness, etc.) for both the serpentines and the coal. This implies that a more in-depth analysis beyond the simple generalization is required. Nevertheless, there seems to be a consensus that the magnitude of the mining operation is of a manageable scale, being of comparable scale of existing commercial mines for minerals like copper.

When dealing with such a large volume of material, transportation becomes an important consideration. It seems probable that mineral sequestration would need to take place at the mine-mouth. This is even more likely when one considers that the silica and carbonates formed by the reactions would be stored back into the mine. This adds a geographic constraint to mineral sequestration strategies, similar to those for ocean and geologic sequestration.

One issue that has not been discussed very much by mineral sequestration proponents is the environmental impact of large mining operations. In fact, some proponents make statements like "mineral sequestration guarantees permanent containment and avoids adverse environmental consequences …" (McKelvy *et al*., 2001). In reality, all processes have environmental consequences, and instead of criticizing environmental concerns of other methods (i.e., they leak and may cause environmental harm), the proponents must address the environmental consequences of a large mining operation. The environmental issues are further exacerbated by the fact that the volume of material increases as a result of the mineral carbonation process. In a review by the IEA Greenhouse Gas R&D Programme, they did address these environmental issues, concluding that "the methods for mineral sequestration of carbon dioxide present significant potential for adverse environmental impacts, which are comparable with the issues faced by similar sized modern quarrying/mining operations" (Newall *et al*., 2000).

Permanence

Perhaps the most positive attribute of mineral sequestration is that the storage is permanent and, therefore, the storage has no potential for leaks that could pose safety or environmental risks. However, one should not imply (as mineral sequestration proponents often do) that sequestration options that leak are not useful. Two key questions to ask are:

- Is there economic benefit to temporary storage?
- Are leaks a cause for concern about safety or the environment?

Temporary storage can range from decades (trees) to centuries (ocean) to millennia (geologic). From an economic perspective, many people argue that storage for a thousand years or more should be considered permanent. However, much shorter storage times may also be economically beneficial (Herzog *et al.*, 2002).

The potential for leaks and their impacts is a very active research area, especially for the geologic sequestration community. There is the potential for any geologic reservoir to leak to some degree, but the critical question is whether that will cause any significant impacts to human health and safety or to the environment. Proponents of geologic sequestration think that the results of this research will show that any leaks can be managed.

In summary, permanence is a very positive attribute for a sequestration technology, but not a necessary one. If all other things are equal, permanence will win out. But since all other things will not be equal, choices will come down to trade-offs, such as cost vs. permanence.

Costs

Since a commercially viable reaction pathway for mineral sequestration has not been identified, it is very hard to do a detailed cost estimate. However, some numbers have been reported, and they are presented below.

Cost estimates used by the proponents of mineral sequestration are $70 per tonne of CO_2 sequestered if one scaled up current laboratory processes. Eliminating pre-treatment and solving the dewatering problem would reduce the cost to $30 per tonne of CO_2 sequestered.

The IEA Greenhouse Gas R&D Programme (Newall et al., 2000) estimates the cost of the current mineral sequestration processes at $60-100 per tonne of CO_2 sequestered, which matches well with the proponents' estimates. By comparison, the IEA GHG R&D Programme reports values for ocean and geologic sequestration at $1-5 per tonne of CO_2 sequestered. All the above numbers are exclusive of any capture and transport costs.

The following points will give the above numbers some perspective:

1. Capture and transport costs need to be added to all the above sequestration costs. A rough estimate of capture and transport costs is $50-60 per tonne of CO_2 avoided.

2. The above sequestration costs need to be put on an avoided cost basis. If a process is energy intensive (such as pre-treatment of the ore), the cost per tonne avoided could be significantly larger than the cost per tonne sequestered.

3. One way to reduce the cost of mineral sequestration is to integrate it with a capture process. This is what ZECA attempts to do.

4. Another option being investigated to improve the economics of mineral sequestration is to find commercial uses for the process by-products.

Conclusions

All new technologies proposed to help mitigate potential climate change can be characterized by a set of plusses and minuses. Proponents of a given technology have the natural tendency to promote the positives of their technology, while highlighting the negatives of potential competitors. At one extreme, one could dismiss most proposed mitigation technologies because of the significant challenges they need to address to become commercial. However, this approach would be unproductive in achieving the ultimate goal of mitigating climate change through the adoption of advanced technologies.

A more prudent strategy is to adopt a portfolio approach. By working on a number of different approaches to the problem, the odds are good that some items in the portfolio will be successful. In the field of carbon sequestration, options include numerous types of geologic sequestration, ocean sequestration, and terrestrial sequestration in addition to mineral sequestration. All are important to investigate. The final mix of these technologies is impossible to predict. However, all may play a role to varying degrees and new strategies may develop that are hybrids of these approaches. For example, *in situ* carbonation can be very helpful to geologic sequestration. Also, using carbonation reactions in conjunction with ocean sequestration is being actively investigated.

For mineral sequestration, the critical challenge is to improve carbonation reaction kinetics in order to develop an economically acceptable commercial process. All other challenges, such as dealing with the environmental issues of a large mining operation, seem manageable.

In conclusion, mineral sequestration is important to include in a portfolio of carbon management and sequestration options. How much priority it should receive compared to other sequestration options is a matter of debate. In my opinion, compared to other sequestration options, mineral sequestration should be viewed as longer-term and higher risk option because it still requires some key fundamental advances (i.e., reaction pathways) that may or may not be achievable in a cost-effective manner.

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[1] Electronic copies of these references (except numbers 2, 8 and 11) can be obtained be e-mailing Howard Herzog at hjherzog@mit.edu - please specify papers by their number.

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Appendix 1

DG^{o}_{f} (KJ/mole) of Selected Carbon Containing Compounds

This table lists the free energies of formation for selected carbon containing compounds. Compounds with lower free energies of formation are more stable from a thermodynamics viewpoint. However, other considerations such as kinetics must be considered when designing processes to convert from one compound to another.

C_6H_6 **(+130)**

CH_4 **(-51)**

HCHO **(-102)**

CO **(-137)**

CH_3OH **(-166)**

HCOOH **(-361)**

NH_2COOH **(-364)**

CO_2 (g) **(-374)**

CO_2 (aq) **(-386)**

$CO_3^{=}$ (aq) **(-527)*** *Need: water to supply energy of hydration

HCO_3^{-} (aq) **(-586)***

$C_2O_4^{=}$ (aq) **(-671)***

$CaCO_3$ (s) **(-1130)**** **Need: alkali to supply neutralization energy

Sources: CRC handbook of Chemistry and Physics (1986-87).
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Appendix 2

Calculation of Mineral Requirements

1. ***Stoichiometric requirement.*** Starting with serpentine ore, $Mg_3Si_2O_5(OH)_4$, we can calculate the stoichiometric amount required per tonne of CO_2 based on the following reaction:

$$1/3Mg_3Si_2O_5(OH)_4 + CO_2 = MgCO_3 + 2/3SiO_2 + 2/3H_2O$$

(? mols serpentine/ mol CO_2) x (mol CO_2/44 g CO_2) x (277.1 g serpentine/ mol serpentine) =
2.1 g serpentine/ g CO_2 =
2.1 tonnes serpentine per tonne of CO_2

2. ***Process requirement.*** For the more practical case, to calculate the tonnes of magnesium silicate ore needed per tonne of CO_2 stored (i.e., sequestered), the following assumptions are taken from Goldberg *et al*. (2001): 40% by wt. MgO content in the ore, 90% ore recovery and 80% conversion of the carbonation reaction.

(1 mol MgO/ mol CO_2) x (mol CO_2/44 g CO_2) x (40.3 g MgO/ mol MgO) x
(g ore/ 0.4 g MgO) x (1/ 0.9) x (1/0.8) =
3.18 g ore/ g CO_2 =
3.18 tonnes ore mined per tonne CO_2 sequestered

3. ***Process requirement compared to coal.*** To calculate the amount of ore needed to sequester all the carbon from a given amount of coal, assuming the coal is 70% carbon:

(3.18 tonne ore/ tonne CO_2) x (44 tonnes CO_2/ 12 tonnes C) x (0.7 tonnes C/ tonne coal) =
8.2 tonnes ore mined to sequester all the carbon released by burning a tonne of coal