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THE NEED AND OPTIONS AVAILABLE FOR PERMANENT CO₂ DISPOSAL

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Summary: Inexpensive, readily available energy is the cornerstone of modern society and the basis of a decent standard of living. The high probability of future restrictions on CO₂ emissions has put in question the use of fossil fuels, the largest, most convenient, and most cost-effective energy resource available. The rapidly growing world population, the need for an improved standard of living worldwide, and the nearly linear dependence of the standard of living on energy consumption, all coupled with the magnitude of today's CO₂ emissions point to an impending crisis. We briefly review the problem and look at the available options. We conclude that for the foreseeable future, fossil fuels will continue to dominate the world energy market, but that CO₂ disposal will be required. Of the possible disposal options, mineral sequestration of CO₂ appears as an extremely promising, permanent, and environmentally benign disposal option.

Introduction

Abundant, clean, low cost energy is critical to the future of not only the U.S., but also the world as a whole. Present day energy sources at best provide only two of these three properties. If environmental impact would not limit energy production, cost and abundance became the driving terms. Fossil fuels are by far the lowest cost energy source currently available, today they account for ~85% of the world's energy supply. After some concern about their long-term availability in the past decades, it is now realized that there are sufficient reserves to last for centuries to come. For instance, global coal reserves are put at 10,000 gigatons (Gt)^[1], whereas the world's yearly consumption of carbon is only ~6 Gt. The only remaining issue for fossil fuels today is their environmental impact, in particular, the large CO₂ emissions resulting from their use. The emissions will continue to grow rapidly as the world population roughly doubles in the next 50 years and it strives to achieve, if not exceed, the standard of living found in the U.S. today. In turn, the effects of CO₂, which include global warming, ocean acidification, and ecological change, will also increase well beyond a non-negligible level. To set the scale, the atmospheric CO₂ concentration has risen by 30% over its pre-industrial age value of 280 ppm to over 365 ppm today. Yearly increases are accelerating from their present value of 1.7 ppm/yr and would already be ~3 ppm/yr were it not for a rather large driving force that drives the CO₂ level back towards its pre-industrial equilibrium value. The size of the associated sinks and their capacity is currently not well known.

The competitors to fossil fuels face their own problems. The promise of unlimited nuclear power, too cheap to meter, has never come to pass, and today in the U.S., nuclear power is a factor of ~2 more expensive than fossil power. Nuclear power also faces environmental issues of its own, which still remain unaddressed. Furthermore nuclear power creates serious proliferation problems and is opposed by a substantial fraction of the U.S. population. Despite these problems, some other countries have adopted nuclear power. These countries typically view a lack of domestic fuel as a more pressing problem. When coupled with the spiraling fossil fuel prices of the 70's the decision to adopt nuclear power was not difficult for these countries. Given that fossil fuel reserves are abundant in the U.S., that the price escalation of the 70's was not permanent, and that there are widespread public concerns that

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Figure 1. The relation between energy consumption and GDP, which is essentially equivalent to wealth^[2]. Although plotted on a log-log scale, the relation is indeed linear as shown by the line which corresponds to 23¢ of GDP/kW-hr of raw energy consumption. Even though there is a scatter of about a factor of 2 for the individual points, the overall relation is valid over two orders of magnitude.

hydroelectric and wind, which rely on natural energy concentrators, are too scarce to satisfy global energy demand. Thus, they do not provide a viable solution to the overall problem.

exist about nuclear power, the main purpose that nuclear power serves today is to set an upper price bound. For fossil fuels to remain viable, their cost including CO₂ disposal must remain under that of nuclear power and all other alternative energy sources. Of course, it is possible that nuclear energy becomes more attractive with technology improvements. However, the same can be said for fossil energy, which starts from a much better economic position.

Most renewable energy sources are more expensive than nuclear power and thus are at an even greater disadvantage. The majority of renewable energy forms ultimately derive their energy from sunlight. The energy density in sunlight is very low. This is further aggravated by the low conversion efficiencies of most solar collectors (photoelectric devices ~ 10–15% efficient, plants ~ 1% efficient). The more price competitive renewable energy sources such as

Attempts to use biological means to achieve disposal of anthropogenic CO₂ will at best provide temporary relief. Biological approaches will have a huge impact on the environment if they attempt to address the full scale of the future problem. Photosynthesis requires energy to turn CO₂ into organic carbon. The energy required is more than is obtained in the combustion of coal. Given the dilute nature of sunlight (~200 W/m² global average) and the typical efficiency of plants to sink carbon (~1%), anthropogenic CO₂ emissions that are 10 times that of today would require an area of almost 1/15th of the world total surface area. As atmospheric CO₂ levels were in equilibrium before the industrial revolution, attempts to store large amounts of additional carbon as biomass will take one away from the natural biological equilibrium that had existed previously. Unless biomass is sequestered itself, for example in the deep ocean, biological solutions will have to artificially maintain a level of stored biomass that is substantially higher than the natural level. This would imply a legacy for future generations who would have to continuously pay for today's carbon dioxide emissions.

Low cost energy is imperative not only from a competitive point of view, but more importantly it is the generator of wealth, as energy is used to produce virtually all products. This is illustrated in Fig. 1, where it is shown that there is a linear relation between energy consumption per person and gross domestic product (GDP) per person. The relation holds over several orders of magnitude, from the richest to the poorest countries. It is the poor countries that can least afford high energy prices as they have little money to spend on energy supply. An immediate corollary is that with increasing energy prices, poorer countries will have an ever more difficult time extracting themselves from poverty. These countries, which dominate the world population, are the ones that most desperately need low energy

prices. Due to their large populations, they will also in time be the world's dominant energy consumers and therefore CO₂ emitters. If CO₂ disposal is not low cost, it will not be adopted by the poorer countries who would be tempted to adopt the cheapest solution which is to emit the CO₂ into the atmosphere.

The task before us is to find a means of disposing CO₂ from the combustion of fossil fuels at a cost that keeps fossil energy competitive with all major alternative energy sources. This will be demanded by the free market economy. In addition to low cost, any proposed solution for disposing of CO₂ must have the following additional features:

- Acceptable to the population at large,
- Able to deal with the scale of fossil fuel reserves,
- Provide a permanent means of disposal (leave no legacy issues for future generations),
- Consume little or no net energy, and
- Be environmentally sound.

For the last item, it is important to emphasize that this must really be measured on a relative scale. Given the scale of global energy consumption and its likely substantial increase in the future, any energy source will have a measurable impact on the environment; the relevant concern is the relative size of the impact.

Mineral CO₂ Disposal

It was suggested by Seifritz^[3] that it might be possible to dispose of CO₂ in the form of mineral carbonates. We have investigated this option in considerable detail and find it is indeed an extremely promising option. Mineral sequestration is a disposal option that achieves the criteria put forward in the above section.

CO₂ reacts exothermically with silicates of alkaline earth metals to form thermodynamically stable carbonates that are environmentally benign. The carbonation reactions are actually part of the natural carbon cycle and huge deposits of stable carbonates exist in the form of magnesium and calcium carbonates. Magnesium and calcium ions are also responsible for most of the CO₂ storage in the oceans, without the otherwise associated lowering of pH. In nature, the carbonation reactions operate on a time scale much too slow to deal with current manmade emissions.

The silicates of alkaline earth metals are of particular interest due to their large abundance in the Earth's crust^[4]. After more careful evaluation^[5], we have chosen to pursue magnesium silicates, as these are available in huge deposits throughout the world^[6]. Furthermore, the magnesium silicate deposits contain a very large weight-percentage of magnesium oxide (35-50%), which is the basic component needed to form the carbonate. Magnesium silicates of interest are olivines and serpentines. The deposits are sections of the oceanic crust/upper mantle, which were thrust up onto land. As such, they are found in extensive deposits at present and former continental boundaries as shown in Fig. 2. The most prevalent useful silicate deposits are in the form of serpentinite, which is a relatively soft rock. The nature and hardness of the deposits make them suitable to open pit mining. The mining and initial ore processing operations that are involved are similar to that in the copper industry. The scale of an operation required for a 1 GW coal-fired power plant operating at 33% efficiency is nearly identical to that of large open pit copper mines currently in operation^[7]. It is also important to note that the serpentine mining operation, in terms of earth moved, is less than 1/3 the size of the strip mining operation typically required to

Figure 2. Known major peridotite or serpentinite deposits. As can be seen, the deposits tend to lie along continental margins or former continental boundaries.

obtain the coal that feeds the power plant. In terms of surface area disturbed, it is even smaller given the large thickness of typical serpentinite deposits relative to coal deposits. Based on the volumes involved and the cost of the combined operations of mining, crushing, milling, and disposal of the tailings in the copper industry, which are very similar to the needed up front processing for the CO₂ disposal operation, one can derive an estimate of \$9/ton of CO₂ disposed for this part of the operation. To set the scale, CO₂ disposal costs of \$10/ton amount to a cost increase of ~1¢/kW-hr in the price of electricity generated by a power plant operating at 33% efficiency. (Doubling the power plant efficiency would cut that cost in half.)

The products of the carbonation reaction would be disposed of back into the mine. For the typical conical shape of an open pit mine, the resulting rise of elevation at the surface of the mine (due to volume change during carbonation) would be rather minor even if one allows for substantial volume increases. These increases are in part due to the increased mass of the carbonate and in part due to the unavoidable increase in pore volume stemming from the processing of the material.

Based on these arguments, mining is not the key impediment to mineral disposal of CO₂. Rather, the real issues revolve about the chemistry involved in the carbonation process. For serpentine, the net reaction of interest is

The end products are natural materials already found in large deposits worldwide. The basic consideration is that of cost, which in turn is set by the kinetics of the reaction, the cost of the required processing equipment, the cost of any required make-up feedstock other than serpentine, and the possible need for external energy input.

We have established one reaction series as a proof of principle which showed that the overall carbonation process can be carried out in a useful and affordable time frame^[8]. The reaction series is

Figure 3. Material and heat flows for the aqueous HCl mineral carbonation process for a coal-fired 1 GW electric power plant assumed to run at 33% efficiency. Coal strip mining is assumed. The indicated heat flows are idealized values. The input heat is likely to be considerably greater than given and only a fraction of the output heat will be useful.

based on the dissolution of the serpentine in a hydrochloric acid bath to yield MgCl_2 along with water and silica. Through a series of steps, the hydrochloric acid is recovered for reuse and $\text{Mg}(\text{OH})_2$ is formed and subsequently carbonated. The material and heat flows for this process are shown in Fig. 3. Although the kinetics of this process have been shown to be favorable, the process is found to require substantial inputs of external energy in spite of the fact that it is exothermic overall by 63.6 kJ/mole CO_2 for pure serpentine. The need to input external heat is due to the loss of otherwise useful heat by the aqueous and therefore necessarily low temperature steps, the repeated need to remove water by evaporation, and the deep energy well of the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, which is a necessary intermediate product. We have examined the thermodynamics of the hydrated MgCl_2 system over a broad temperature and pressure range in a series of internal reports^[9,10,11], which are partially summarized in a recent conference presentation^[12]. This analysis identifies the limiting step in terms of heat input as the partitioning of $\text{Mg}(\text{OH})\text{Cl}$ into $\text{Mg}(\text{OH})_2$ and $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$, which, regardless of temperature and pressure, is found to require a value of at least 6 for n .

While investigating the overall $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ system we identified various alternative reaction routes including reduced water versions of the aqueous process and molten salt processes. Although considerable reductions in the need for external energy input were achieved for the reduced water aqueous processes, a version that required no external energy input was not found. However, a slightly hydrated ($n = 1-2$) molten salt process was identified from which net heat could in theory be extracted. The process is sketched in Fig. 4 and takes place as a continuous process in a single reaction vessel. The process relies on the existence of a significant partial pressure of HCl which is built up in the melt at higher temperatures ($\sim 300^\circ\text{C}$) as an equilibrium is established between $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ and $\text{Mg}(\text{OH})\text{Cl} +$

Figure 4. A schematic diagram of the molten salt process.

HCl. Although the thermodynamics do not quite favor the self-sustaining dissolution of serpentine in such a melt, this situation is nearly achieved as the Gibbs free energy for this process approaches zero. Thermodynamic calculations show that the simultaneous introduction of a substantial CO_2 partial pressure (20-30 atm) does result in a self-sustaining reaction, provided the CO_2 partial pressure is maintained. In such a situation, the CO_2 reacts with the MgCl_2 and water to yield MgCO_3 and HCl, the latter being recycled. In this process the starting, slightly hydrated, MgCl_2 molten salt is not consumed. Instead, it effectively acts as a catalyst, and in all likelihood provides the kinetics typically associated with molten salt reactions. The predictions of the thermodynamic calculations have yet to be established. We are just beginning to experimentally investigate this process. The corrosive nature of the process coupled with the

required elevated temperatures and pressures has limited the work achieved to date. Additional issues that will need to be addressed include the continual dilution of the salt by the water produced from the serpentine, the required separation of the SiO_2 and MgCO_3 from the molten salt, the corrosive nature of the process, and the potential formation of various sordid cements^[13].

Another reaction process that we are pursuing is the direct gas solid reaction between CO_2 and serpentine, or some of the decomposition products of serpentine. At temperatures of $\sim 500^\circ\text{C}$ and pressures of ~ 300 atm, the reaction proceeds rapidly to completion. As the reaction takes place in a single step, heat extraction is again possible. Furthermore, unlike the molten salt process, in this case the end products are pure and thus no separation steps are needed. The issue that remains to be addressed is the needed lowering of the pressure, which is required to make the process economical. This must be done without compromising the kinetics that are achieved at the higher temperatures allowed by the higher pressures. (MgCO_3 become unstable, decomposing into MgO and CO_2 at these temperatures when at lower pressures.)

As a final route for mineral sequestration we are looking at the feasibility of using underground disposal through the injection of supercritical CO_2 . Unlike conventional underground CO_2 disposal options, our goal is to choose appropriate injection sites where the CO_2 is able to chemically bind with the strata into which it is injected. Such an approach would again yield permanent disposal of the CO_2 , unlike other underground disposal options where there always exists the potential for the CO_2 to escape at a later date. This idea was pursued for a short period of time^[14,15], but before a thorough understanding of the feasibility of this option could be established, the work stopped due to a lack of funding. This underground disposal option opens up additional areas for CO_2 disposal given that much lower concentrations of the appropriate binding minerals are now allowable. The allowable time scale for the carbonation reactions also becomes much longer than in an industrial process. Ideally one would like

reaction time constants that are measured in years; long enough to allow the CO₂ to spread a considerable distance from the injection site, yet short enough to avoid any long-term legacy problems.

Summary

We have outlined the need for abundant, clean, low cost energy, and the reasons why energy consumption will rise rapidly in the future. The faster the rise in the standard of living worldwide, and thus the faster the rise in energy usage, the better for the world population as a whole. Fossil fuels will continue to dominate the world energy market given their low cost and abundant supply. The issue that must be addressed is the rising atmospheric and oceanic CO₂ levels associated with their use. Mineral carbonation of alkaline earth silicates is a viable solution to this problem. It offers a permanent disposal option for the carbon dioxide that can cope with the full scale of the problem, at what will hopefully be affordable costs. Several different routes for achieving the carbonation reactions have been presented and will continue to be investigated.

References

- ¹ United Nations, *1991 Energy Statistics Yearbook*, New York (1993).
- ² These data are taken from Hoffert and Potter (*Engineering Response to Global Climate Change*, R. G. Watts, Ed., Lewis Publishers, New York, 1997) as they derived them from Hammond (*World Resources 1990-91*, Oxford University Press, NY, 1990).
- ³ W. Seifritz, "CO₂ disposal by means of silicates," *Nature*, **345**, 486 (1990).
- ⁴ A. H. Brownlow, *Geochemistry*, Prentice-Hall, Englewood Cliffs, NJ, (1979).
- ⁵ Fraser Goff and K. S. Lackner, "Carbon Dioxide Sequestering Using Ultramafic Rocks." *Environmental Geosciences*, **5**, #3 (1998), pp. 89-101.
- ⁶ R. G. Coleman, *Ophiolites*, Springer-Verlag, Berlin: (1977).
- ⁷ Klaus S. Lackner, Darryl P. Butt and Christopher H. Wendt, "Magnesite Disposal of Carbon Dioxide," The Proceedings of the 22nd International Technical Conference on Coal Utilization & Fuel Systems, March 16-19, 1997, Clearwater, Florida, U.S.A., pp. 419-430.
- ⁸ Klaus S. Lackner, Darryl P. Butt & Christopher H. Wendt, "Progress on Binding CO₂ in Mineral Substrates," *Energy and Conservation Management*, **38** Suppl, S259-S264, (1997).
- ⁹ C.H. Wendt, D.P. Butt, K.S. Lackner, and H-J Ziock, "Thermodynamic Calculations for Acid Decomposition of Serpentine and Olivine in MgCl₂ Melts- I: Description of Concentrated MgCl₂ Melts," Los Alamos National Laboratory Report, LAUR-98-4528, July 27, 1998, 22 pp.
- ¹⁰ C.H. Wendt, D.P. Butt, K.S. Lackner, and H-J Ziock, "Thermodynamic Calculations for Acid Decomposition of Serpentine and Olivine in MgCl₂ Melts- II: Reaction Equilibria in MgCl₂ Melts," Los Alamos National Laboratory Report, LAUR-98-4529, October 7, 1998, 28 pp.
- ¹¹ C.H. Wendt, D.P. Butt, K.S. Lackner, Raj Vaidya, and H-J Ziock, "Thermodynamic Calculations for Acid Decomposition of Serpentine and Olivine in MgCl₂ Melts- III: Heat Consumption in Process Design," Los Alamos National Laboratory Report, LAUR-98-5633, November 25, 1998, 23 pp.
- ¹² Christopher H. Wendt, Darryl P. Butt, Klaus S. Lackner & Hans-Joachim Ziock, "Thermodynamic Considerations Of Using Chlorides To Accelerate The Carbonate Formation From Magnesium Silicates," to appear in the proceedings of the Fourth International Conference on Greenhouse Gas Control Technologies, Interlaken, Switzerland, August 30 - September 2, 1998.
- ¹³ W. F. Cole and T. Demeduck, *Aust. J. Chem.*, **8** (1955), 234.
- ¹⁴ E.H. Perkins and W. D. Gunter, "Mineral traps for carbon dioxide," in *Aquifer Disposal of Carbon Dioxide, Hydrodynamic and Mineral Trapping - Proof of Concept*, Brian Hitchon (editor), Geoscience Publishing Ltd., (1996), 93-113.
- ¹⁵ W. D. Gunter, B. Wiwchaw and E.H. Perkins, "Autoclave experiments and geochemical modeling," in *Aquifer Disposal of Carbon Dioxide, Hydrodynamic and Mineral Trapping - Proof of Concept*, Brian Hitchon (editor), Geoscience Publishing Ltd., (1996), 115-141.