

CARBONATE CHEMISTRY FOR SEQUESTERING FOSSIL CARBON

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■ **Abstract** Fossil fuels play a crucial role in satisfying growing world energy demands, but their continued use could cause irreparable harm to the environment. Unless virtually all anthropogenic carbon dioxide is captured, either at the source or subsequently from the air, and disposed of safely and permanently, fossil fuels may have to be phased out over the next few decades. Sequestration of waste carbon dioxide will require methods that can safely store several trillion tons of carbon dioxide. Long-term storage of a gaseous substance is fraught with uncertainty and hazards, but carbonate chemistry offers permanent solutions to the disposal problem. Carbonates can be formed from carbon dioxide and metal oxides in reactions that are thermodynamically favored and exothermic, which result in materials that can be safely and permanently kept out of the active carbon stocks in the environment. Carbonate sequestration methods require the development of an extractive minerals industry that provides the base ions for neutralizing carbonic acid.

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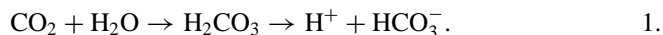
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INTRODUCTION

Providing a decent standard of living to 10 billion people is one of the great challenges mankind will face in the twenty-first century. Meeting this challenge requires continued access to large amounts of energy. Fossil carbon has fueled the world economy for the last two centuries, and carbon resources are likely to last for several more. However, carbon dioxide cannot be allowed to accumulate in the atmosphere. A continued reliance on fossil fuels would require the capture of carbon dioxide, either at the point of generation or from the air, followed by its permanent and safe disposal.

Managing anthropogenic carbon fluxes depends on the safe storage of trillions of tons of carbon dioxide. This review focuses on technological approaches that take advantage of the fact that carbon dioxide is the anhydrous form of carbonic acid,



Neutralizing this acid with readily available alkali or alkaline earth compounds, which leads to the formation of carbonates and bicarbonates, is thermodynamically favored. These products tend to be chemically stable and environmentally benign. Chemical pathways involving carbonic acid and its carbonate and bicarbonate salts open a number of possibilities for capture and most importantly for the permanent and safe disposal of carbon dioxide.

Carbonate chemistry has been studied for centuries, but for carbon management, this review will only deal with the simplest of concepts. Forming carbonates for sequestration of carbon dioxide is a new idea, and even simple concepts still need to be explored. For example, using mineral silicates to form carbonates in an engineering context was first mentioned in 1990 (1) and studied in detail in 1995 (2). The idea of forming carbonates from saline brines for the purpose of carbonate sequestration was suggested in 1992 by Dunsmore (3). However, in the context of

natural weathering processes, it has been known for a long time that carbonic acid is removed from the air as it is neutralized by forming bicarbonates from carbonate rocks or alternatively by extracting alkaline materials from silicate rocks (4).

This review will survey the possibilities inherent in carbonate chemistry and put them into the context of the broader goal of carbon sequestration. It will summarize research in carbonate based sequestration technologies and point to ideas and concepts that have not yet been explored in great detail. With such a broad scope, the paper is bound to be incomplete and biased by the experience of the author. Rather than tabulating and reviewing previous research, my goal is to sketch out concepts and present a coherent view of carbonate chemistry as a means of preparing waste carbon for permanent and safe disposal. Carbonate sequestration encompasses a far larger set of options than those that have been considered so far by the few researchers in the field. My hope is to stimulate a debate that could advance and shape a nascent field of earth engineering (5, 6).

At first sight, carbonate chemistry-based approaches appear more complex and more costly than other methods of carbon sequestration. However, one must consider that a net-zero-carbon economy may need to sequester tens of billions of tons of carbon dioxide on an annual basis. It is easy to store a small amount of carbon dioxide for a short time, but considering the size of the fossil fuel resources, trillions of tons may need to be stored, and storage will need to last for millennia, not just decades or centuries. It is on these scales that the advantages of carbonate chemistry come to bear.

This review centers on the disposal of carbon, even though capture and transport of carbon dioxide are often viewed as more difficult (7, 8). However, the view represented by Herzog & Drake (8) and Taylor et al. (9) is too focused on a transition phase, and it ignores the scale on which carbon dioxide sequestration will have to operate. It is indeed difficult to capture carbon dioxide in existing power plants, and doing so would greatly reduce energy efficiency and raise costs. Costs and energy penalties will be reduced once carbon capture is fully integrated into the power plant's design. The greatly reduced costs in sulfur remediation suggest that the price of a new technology can be driven down if the appropriate incentives are in place (9).

On the other side of the ledger, small-scale disposal of carbon dioxide has a multitude of cheap options. Thus, it is easy to see why initially this part of the problem looks easy. As the scale of sequestration grows and gradually encompasses carbon from all fossil fuel uses, finding long-term, permanent storage becomes more challenging. The exploration for new reservoirs, their characterization, and their continued monitoring and management need to be fully accounted for in the cost of sequestration. It is likely that these activities will drive the overall cost. The initial underestimation of waste disposal costs in the nuclear industry provides a good analogy for this aspect of the problem.

This article explores the possibility that the world may keep using fossil fuels in increasing quantities for the foreseeable future. There are other paths that the world could follow, but they will not be discussed here. There are two reasons

for exploring the viability of this particular path. First, fossil carbon represents a huge low cost energy resource that, until it runs out, remains a tempting target for economic development. Second, abandoning the present energy infrastructure, or just neglecting to develop it further, would limit access to energy and make the world-wide fight against poverty far more difficult (10, 11).

There are only two compelling reasons for phasing out fossil energy: The environmental impact has such dire consequences that they cannot be tolerated, mitigated, or avoided; or the price of nonfossil energy sources becomes so low that they make fossil energy obsolete. In this review I will argue that technology could eliminate the environmental problems that are of most pressing concern and therefore eliminate the first reason. I will not address the question of whether or when other technologies could economically replace fossil energy. However, the additional cost of making fossil energy environmentally acceptable will increase the competitiveness of other alternatives.

In considering technological options for maintaining access to fossil fuels, this review also does not discuss transitional technologies for carbon management but only considers long-term viability. This is not meant as an argument against transitional technologies. Quite the contrary, these will play an important role. It is important to realize that carbon sequestration could be practiced today, even if it could not yet cope with the full scale of the fossil energy resources. Starting carbon sequestration by any method would buy time, possibly many decades before fossil fuels are either phased out or permanent, large-scale sequestration is fully implemented. The choice will depend on the availability of long-term options for carbon sequestration.

THE CARBON PROBLEM

Over the next one hundred years, the combustion of fossil fuels could inject amounts of carbon dioxide into the atmosphere that are large compared to the uptake capacity of natural sinks (12). This will have environmental consequences, the most prominent being climate change. Carbon dioxide in the atmosphere is also in close contact with other active carbon pools in the oceans, terrestrial soils, and biomass. These reservoirs readily exchange carbon and, at least near their interfaces, they equilibrate rapidly (13). Annual exchanges between reservoirs far exceed anthropogenic contributions. Consequently, the impacts of fossil fuel use are not limited to the atmosphere but include, among others, the acidification of the surface ocean and direct CO₂ fertilization of oceanic and terrestrial ecosystems (13, 14).

Carbon dioxide is not just a potent greenhouse gas. It is chemically reactive and physiologically active. The same carbonate chemistry that could support carbon management asserts itself in many interactions of carbon dioxide with the environment. A well-established consequence of excess carbon dioxide in the air is the acidification of the surface ocean, which causes a reduction in the carbonate ion concentration. Doubling CO₂ in the air would not only lower the pH of surface

ocean water by 0.3, but it would also reduce the carbonate ion concentration by a factor of two (15). Recent experimental data suggest that the reduction in carbonate ion concentrations greatly affects the growth rate of coral reefs (16, 17).

Future Carbon Demand

The Energy Information Administration estimates a growth in world energy consumption of 60% between 1999 and 2020 (18), or 2.3% per annum. Sustaining this growth rate for 100 years with the current fossil fuel mix would drive total emissions to 2300 GtC for the century. Compared to most Intergovernmental Panel on Climate Change (IPCC) scenarios (19), this would be aggressive growth. Nevertheless, the per capita carbon consumption of 10 billion people in 2100 would still be less than that of U.S. consumers today. Projected growth of energy consumption in the twenty-first century would also fall short of the actual growth in the twentieth century. If the anticipated improvements in energy intensity fail to materialize or if economic development is more vigorously pursued than anticipated, these numbers could, however, prove to be on the low side.

Resource Size

Continued growth in fossil fuel consumption would not be stopped by resource limitations. Coal resources alone are estimated above 10,000 Gt (20), with proven economic reserves at about 1000 Gt (21).

If methane hydrate deposits prove to be economically extractable, carbon reserves may turn out to be far larger. Methane hydrates might contain as much as 50,000 Gt of carbon (22). If a substantial fraction of this carbon could be extracted, the limiting resource may well be oxygen. In terms of mass, fossil power generation consumes three to five times as much oxygen as carbon. Two hundred thousand Gt O₂ would represent 20% of the atmosphere's oxygen. Once removed, it could not be easily resupplied. Photosynthesis, for example, could not replenish the depleted oxygen stocks because in order to do so biomass stocks would have to grow by two orders of magnitude.

Because the different forms of fossil carbon are readily interchangeable, the world does not depend on one particular form of fossil energy. Ten thousand Gt of carbon in any form assure energy availability for more than a century. Examples of interchangeability exist already and not only in the electricity sector. Synthetic crude oil from tar sand is economically competitive with conventional crude oil (23). SASOL, the South African company that produced synthetic gasoline from coal, has shown that coal liquefaction is feasible and not greatly more expensive than gasoline from oil (24). An increase in production scales from South Africa's market to the world market would most likely result in substantial cost reductions. It could drive the cost of liquefaction well below typical oil prices in the \$20 to \$30 per barrel range. Recent cost estimates suggest that coal gasification, coproducing electric power, and Fischer Tropsch liquids could already be competitive as long as crude oil prices stay above \$30 per barrel (25). Consequently, one can safely

assume that hydrocarbon energy will remain available for the foreseeable future and that its cost, even though it may be subject to short-term price swings, will not be driven upward by resource limitations (20).

Limitations of Natural Sinks

Absorbing 2300 Gt of carbon by natural processes without environmental consequences is not possible. The atmosphere, biomass, soil, and ocean are all limited in their uptake capacity. As an example of the difficulties one might encounter, consider the debate over the ecological consequences of fuel accumulation through fire suppression in the western United States (26). Fire suppression is often considered ecologically detrimental, but it does play a substantial role in the overall carbon balance in the United States (27). Yet a worldwide 30% increase in biomass, which would be difficult to sustain, would sequester only 200 Gt of carbon. Similar constraints would make it equally difficult to sustain a substantive increase in soil carbon. A few hundred gigatons added to a 1500 Gt reservoir of carbon would be optimistic. These approaches to carbon sequestration would demand active maintenance of carbon stocks for generations. Returning to preindustrial biomass and soil carbon levels should be possible, but it would hardly affect the overall carbon balance. Biomass and soil carbon changes in the past were already dwarfed by past fossil carbon emissions that were far smaller than those expected in the coming century.

The oceans' uptake capacity for carbon dioxide is also relatively small. As discussed below, stirring 1500 Gt of carbon as carbonic acid into the ocean would lower its pH from top to bottom by 0.3. Realistically, one could only reach a fraction of the ocean, and most parts of the ocean would return the excess to the atmosphere in a few hundred to a thousand years, which is too short for long-term carbon storage. Consequently, storing more than an additional 300 to 600 Gt of carbon in the ocean without adding alkalinity is not likely.

The natural reservoirs that are in close contact with the air and that are ecologically active will simply not be able to take on the excess carbon that human activities could generate over the course of the next century. The past carbon injection, approximately 300 Gt, was still small compared to the overall uptake capacity of the system. This century's emissions most likely will be large by this measure. Unless fossil fuels will be abandoned, carbon management will be required to divert a large fraction, if not all, of the carbon away from the mobile, interconnected carbon pools on the surface of the Earth.

Time Scales for Carbon Storage

Disposing of the carbon that might be consumed over the next one or two centuries and sequestering it away from the ecologically active stocks would require storage of trillions of tons of carbon. The bigger the volume of stored carbon dioxide, the longer it needs to be stored. If there is a maximum sustainable rate F_c of carbon injection into the atmosphere or the closely coupled surface pool, the leakage rate

from carbon storage should be kept below this limit. Otherwise, the excess amount of carbon that escaped from storage would have to be recaptured and disposed of again. Although this may be acceptable on the century scale, on longer scales it would be hard to justify. Storage time, t_s , and stored carbon mass, C_s , are linked through leakage rates

$$t_s \approx \frac{C_s}{F_c}. \quad 2.$$

Consider as a possible scenario the fossil fuel era lasting another 200 years with a total consumption of 5000 Gt of carbon. This would not exhaust fossil fuel resources nor would it raise per capita fuel consumption of the world to today's level in the United States.

In order to prevent a continued rise in atmospheric carbon dioxide concentrations, the leakage rate from the sequestered carbon pool must be small compared to today's carbon dioxide emissions. To be specific let us limit leakage arbitrarily to less than 2 Gt C/yr. A leakage rate $F_c = 2$ Gt/yr would imply a minimum storage lifetime $t_s = 2500$ years. Unless sequestration is only to provide time for the orderly phase out of fossil fuels, carbon storage times must eventually be measured in millennia.

Future research will need to establish a definitive upper limit on the allowable leakage rate and the maximum total carbon injection that could be tolerated by the surface pool. For now a rough estimate for century scale emissions is given by the IPCC trajectories for stabilization. They seem to suggest a sustainable emission of roughly 2 Gt of carbon per year at a constant atmospheric carbon dioxide level of 550 ppm (13). Such a number intuitively makes sense if one assumes that the oceans' conveyor, which transports roughly 0.6 Gt of carbon into the deep ocean today, will scale with the excess carbon in the air. Natural sequestration rates would therefore triple at about 550 ppm (T. Caplow, private communication).

In order to sustain a quasi-steady state with roughly 2 Gt of carbon sequestered annually for more than 1000 years, the ocean must remove this carbon from the active pool. Otherwise the carbon dioxide would be reemitted to the air after the ocean has turned over in about a thousand years. The carbon dioxide would be stabilized if for example carbonate sediments on the bottom of the ocean would neutralize the added carbonic acid (29). However, carbonate sinks on the ocean floor are themselves limited, and it is not clear that they could absorb a total of 5000 Gt of carbon leaking from other storage sites at a rate of 2 Gt/yr.

CONSTRAINTS ON ENGINEERED CARBON SINKS

Because dilution of the fossil carbon into the atmosphere and the directly linked natural carbon reservoirs is insufficient to cope with emissions considered likely by the IPCC for business as usual over the next century (19), the only avenue to maintaining the fossil fuel option is to explore other carbon storage sites. These

will need to accommodate the size of the expected carbon emissions and provide safe and permanent storage.

As stated before, this long-term constraint does not preclude a start-up phase in carbon management that relies on lower cost options, which may not have the uptake capacity or long storage times that will eventually be required.

Constraints From Life Time Considerations

The ultimate requirement for millennial storage times will over decades severely limit options for sequestration and disposal. Storage times of thousands of years rule out most biomass, soil, and many ocean disposal options. Turnover times in these reservoirs tend to be measured in terms of years to centuries and would fall short of the millennia required for carbon dioxide storage. I believe it also rules out monitoring as a safeguard against accidental releases. Monitoring may be relied upon for a generation or two but not for hundreds of generations. One should not assume that technological progress and economic growth will continue indefinitely, nor would it be fair to impose maintenance tasks on far distant future generations. Although it is clear that the next few generations would benefit from the additional economic growth that might result from easier access to energy today, it would be difficult to extend this argument 2000 years into the future. Furthermore, the cumulative demands of 100 prior generations on a future society could end up being bigger than even a wealthy society could afford. These challenges are not new; they are similar to those that have been at the forefront of the development of nuclear waste repositories (30, 31).

Constraints From Energy Considerations

As long as fossil fuels are used as energy sources, one cannot dispose of reduced carbon. Figure 1 shows the enthalpy of reaction per mole of carbon for a variety of compounds, which indicates that reduction of carbon dioxide requires an amount of energy comparable to the heat released in its production. By disposing of reduced carbon one also returns the heat of combustion and thus renders fossil fuels useless. This holds true, even if the path toward reducing carbon dioxide is indirect, as for example in the production of synthesis gas from methane and carbon dioxide (32).

A possible exception to the above rule is the disposal of carbon resulting from the partial oxidation of methane to carbon and water (33). Because half of the heat of combustion of methane is derived from the oxidation of hydrogen, it is possible to design power plants that generate power and return solid carbon. However, such an energy technology would leave behind half the energy content of the fuel. Methane consumption would have to double to account for this lowered efficiency of the energy extraction process.

Another possible exception is the formation of biomass for carbon disposal if the energy input from photosynthesis would be viewed as coincidental. Unless one is increasing the size of standing forests, it is hard to see, though, why the biomass produced should not simply displace fossil fuels (3, 34).

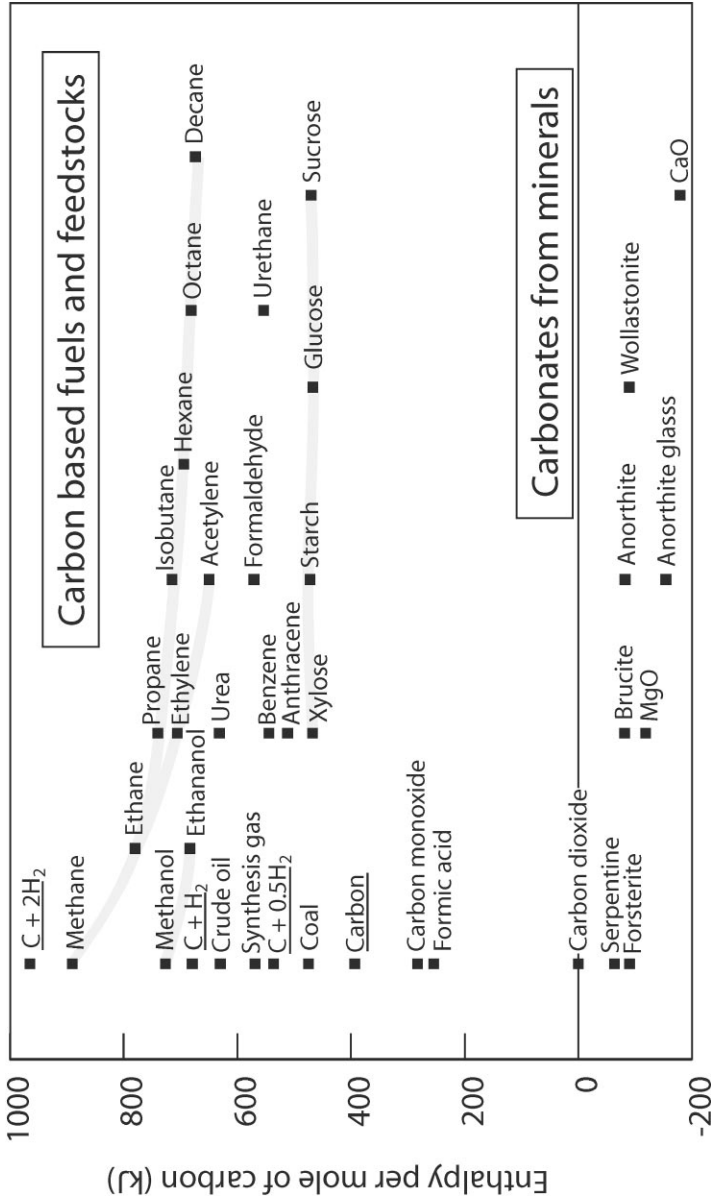


Figure 1 Enthalpy per mole of carbon of various carbon bearing compounds. For the positive entries the enthalpy represents the heat of reaction for the full oxidation of the compound to carbon dioxide and water. By convention the enthalpies of H_2O , CO_2 , and O_2 are zero. The energy of carbon can be reduced below its state in carbon dioxide by letting the carbon dioxide react with various common silicate minerals. The enthalpies at the bottom of the graph represent the enthalpies of reaction when carbon dioxide and the named mineral form the stoichiometrically possible combination of SiO_2 , $MgCO_3$, or $CaCO_3$. In the case of serpentine, H_2O is also among the reaction products. For convenience, these last entries are labeled by the starting product, not the end product.

Long-term storage of solid forms of reduced carbon may well be possible, but the longevity of such storage options has not been thoroughly investigated. As long as coal is mined, it appears counterproductive to bury carbon of similar or higher quality.

With all other options impossible or impractical, one is forced into storing fully oxidized carbon. This leaves open the options of storing carbon dioxide, carbonic acid, carbonates, or bicarbonates.

Physical Constraints on Storing Carbon Dioxide as a Gas or Liquid

Carbon dioxide is a gas, and therefore its long-term storage requires physical barriers to keep it out of the atmosphere. These barriers must be guaranteed for millennia and safely contain gas pockets that over the next hundred years would have to store a mass comparable to that of all the water in Lake Michigan. Containing this gas in a reasonable volume requires pressurization. Good storage sites are therefore likely underground or in the deep ocean where the necessary pressure is easily maintained.

Enhanced oil and gas recovery through carbon dioxide injections into oil or gas-bearing strata provides an attractive option for carbon sequestration that utilizes the carbon dioxide and that could be implemented immediately (35, 36). If the oil is associated with gas, there should be an intact seal over the reservoir that would minimize the risk of carbon dioxide escaping. Furthermore, in enhanced oil or gas recovery, material has been extracted from the formation. Reducing pressure prior to injection of carbon dioxide eliminates over-stressing a formation past natural levels. Otherwise, injection of large volumes of liquid into rock formations either leads to swelling or expulsion of other fluids from the reservoir. These concerns are not trivial, as the volumes involved are very large. At liquid density, the annual output of a conventional gigawatt coal plant (1000 tons of CO₂ per hour) would occupy the volume of a slab of 100 km² and 10 cm thickness.

Surprisingly, the first commercial carbon sequestration project did not utilize the carbon but disposed of carbon dioxide removed from natural gas produced in the North Sea (37). Statoil injects this waste carbon dioxide into the Utsira Formation at Sleipner Field in order to avoid a tax of \$50 per ton of carbon dioxide that Norway levies on certain emissions (38, 39). After injection, the bulk of the carbon dioxide remains a compressed gas or liquid, but the fraction of carbon dioxide that dissolves into the brine in the pore space gradually increases. Conceptually, the difference between dissolved carbonic acid and carbon dioxide is small. Exposed to air, the solution would effervesce and return its carbon dioxide load. Just as for gaseous carbon dioxide, one must maintain a physical barrier that separates the solution from the air. However, the mobility of the dissolved carbon dioxide species is far smaller than that of a separate gas phase. Buoyancy effects that drive gaseous carbon dioxide to the surface would also have been eliminated (40). Indeed water laden with carbonic acid tends to be denser and move downward. The dissolution of

carbon dioxide into pore space water can therefore alleviate many of the concerns over carbon dioxide leakage.

Storage of liquid carbon dioxide in the deep ocean is possible because cold carbon dioxide at a depth below 3000 m is denser than water and would pool at the bottom of the ocean (41, 42). The question here is how much time it would take for such a lake to dissolve into the surrounding water and be carried along with ocean currents. The formation of solid carbon dioxide hydrates or clathrates will help in slowing down the dissolution process. Nevertheless typical estimates suggest that the lifetime of such a lake is only on the order of a few centuries. However, this may strongly depend on the choice of the specific location for the carbon dioxide pool.

Chemical Constraints on Dissolving Carbonic Acid in the Ocean

As long as carbon dioxide concentrations in the air are rising, surface water will take up additional carbon dioxide. It is possible to sequester carbon dioxide in natural water bodies if one is willing to accept a permanently higher level of carbon dioxide in the air. The only reservoirs of significance are the oceans, but they are so large that left to themselves they would take many centuries to equilibrate with the atmosphere and in the process of equilibration absorb 70% to 80% of the excess carbon dioxide.

Injection of carbon dioxide at 700- to 1000-m depth into the ocean represents a strategy of active intervention that aims to eliminate this delay and thereby reduce the atmospheric carbon dioxide peak (43, 44). The combined capacity of the atmosphere/ocean reservoir remains, however, unchanged.

For a simple estimate of the ocean's uptake capacity, consider the Revelle factor R , which is the logarithmic derivative of the partial pressure of carbon dioxide over the ocean with respect to the total dissolved inorganic carbon C at constant carbonate alkalinity A (15, 45) or

$$R = \frac{C}{P_{\text{CO}_2}} \frac{\partial P_{\text{CO}_2}}{\partial C} \Bigg|_{A=\text{const}} = \frac{\partial \ln P_{\text{CO}_2}}{\partial \ln C} \Bigg|_{A=\text{const}}. \quad 3.$$

As can be seen in Table 1, the carbonate alkalinity is approximately equal to

$$A \approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]. \quad 4.$$

Charge neutrality demands that the carbonate alkalinity only changes if other ion concentrations change. This might happen through dissolution of minerals on the ocean floor or dissolution of minerals entering the ocean with continental runoff. Alkalinity therefore only changes on timescales large compared to the turnover time of the ocean (46). Over the few hundred years the fossil fuel era might last, natural processes will not substantially change alkalinity.

Based upon the mean values of the alkalinity, total CO_2 concentration and salinity for the global oceans (47), the mean Revelle factor for the oceans has

TABLE 1 Definition of dynamic variables and parameters that describe the carbonate chemistry of seawater. For numerical values and details on these relations see (15).

| Variable | Symbol | Relations |
|--|----------------------|---|
| Partial pressure of atmospheric CO ₂ | P_{CO_2} | $P_{\text{CO}_2} \sim 3.7 \times 10^{-4}$ atm |
| Dissolved neutral carbon and undissociated carbonic acid | $[\text{CO}_2]$ | $[\text{CO}_2] \approx 10^{-4.7}$ mol/kg |
| Bicarbonate ion concentration | $[\text{HCO}_3^-]$ | $[\text{HCO}_3^-] \approx 10^{-2.7}$ mol/kg |
| Carbonate ion concentration | $[\text{CO}_3^{--}]$ | $[\text{CO}_3^{--}] \approx 10^{-3.8}$ mol/kg |
| Alkalinity | A | $A = [\text{HCO}_3^-] + 2[\text{CO}_3^{--}] + [\text{OH}^-] - [\text{H}^+]$ $A \approx [\text{HCO}_3^-] + 2[\text{CO}_3^{--}]$ |
| Total dissolved carbon | C | $C = [\text{HCO}_3^-] + [\text{CO}_3^{--}] + [\text{CO}_2]$ $C \approx [\text{HCO}_3^-] + [\text{CO}_3^{--}]$ |
| Henry's law constant | K_H | $K_H = 10^{-1.54}$ mol/kg/atm $K_H P_{\text{CO}_2} = [\text{CO}_2]$ |
| First disassociation constant of carbonic acid | K_1 | $K_1 = 10^{-6}$ mol/kg $[\text{HCO}_3^-][\text{H}^+] = K_1[\text{CO}_2]$ |
| Second disassociation constant of carbonic acid | K_2 | $K_2 = 10^{-9.12}$ mol/kg $[\text{CO}_3^{--}][\text{H}^+] = K_2[\text{HCO}_3^-]$ |
| Rescaled pressure | P, k | $P = k P_{\text{CO}_2}$ $k = \frac{K_1}{K_2} K_H = 40$ mol/kg/atm |
| Dimensionless carbonate ion concentration | ε | $\varepsilon = \frac{A-C}{A} \sim \mathcal{O}(0.1)$ |
| Dimensionless alkalinity | γ | $\gamma = \frac{A}{k P_{\text{CO}_2}} = \frac{\varepsilon}{(1-2\varepsilon)^2} \sim \mathcal{O}(0.1)$ |

been estimated to be 15.8 at a mean water temperature of 3.9°C under 1 atm total pressure (T. Takahashi, private communication). For a constant R , the relationship between C and P at fixed A would simplify to

$$P_{\text{CO}_2} = P_{\text{CO}_2}^{(0)} \left(\frac{C}{C_0} \right)^R. \quad 5.$$

At doubled P_{CO_2} , the dissolved inorganic carbon in the ocean would be larger by a factor of $2^{1/15.8}$ or by 4.5%. Starting from a total dissolved carbon of 39,000 Gt currently in the oceans, this would imply an uptake capacity of 1800 Gt. The actual uptake capacity of the ocean is even lower than this simple calculation suggests. Because the Revelle factor increases with P_{CO_2} , a larger value for the Revelle factor should be used. At $R = 18$, the increase in C would be 3.9%. Furthermore, this simple analysis assumes that the equilibrium partial pressure over the water is doubled in the entire ocean volume. However, deeper layers of the ocean are already in equilibrium with a higher value of P_{CO_2} due to the actions of the biological pump (49). By simply doubling the equilibrium P_{CO_2} throughout

the volume of the ocean, one implicitly assumes that the strength of the biological pump doubles with the atmospheric P_{CO_2} . This unrealistic assumption makes the above estimate of the ocean's uptake capacity too large.

The above analysis, even though very simple, makes clear that one cannot use the total dissolved carbon in the ocean as a yardstick for the ocean's carbon uptake capacity. At constant alkalinity A , any increase in the total dissolved carbon,

$$C \approx [\text{HCO}_3^-] + [\text{CO}_3^{--}] \approx A - [\text{CO}_3^{--}], \quad 6.$$

must stem from the replacement of one carbonate ion by two bicarbonate ions. The range over which C can change is limited by the total carbonate concentration, which for seawater is less than 10% of the total dissolved carbon. As the ratio of carbonate to bicarbonate is lowered, the pH of the ocean drops, which limits the amount of change that is environmentally acceptable.

NEUTRALIZING CARBONIC ACID

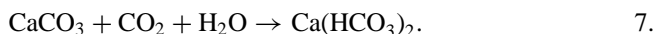
The natural weathering processes eventually remove carbon dioxide from the atmosphere by neutralizing the acid with mineral alkalinity. Carbonate weathering generates bicarbonates, and silicate weathering extracts alkalinity from silicate rock, leaving behind silicates and carbonates or bicarbonates. Carbonate weathering neutralizes the acidic carbon dioxide but keeps it in aqueous solution. The weathering of silicates provides alkaline earth elements that can remove the excess bicarbonate from the ocean by precipitating solid carbonates. This precipitation would restore the biospheric carbon pools to their initial state.

Carbon sequestration strategies based on the formation of carbonate or bicarbonates are accelerating natural weathering processes. There is a large class of sequestration methods that could be developed on this principle. A common feature is that these methods neutralize carbonic acid before or during sequestration. The disposal of carbonates or bicarbonates rather than carbonic acid reduces environmental impacts and raises the capacity, permanence, and safety of potential carbon sinks.

The introduction of bicarbonate salts into the ocean is one of three major carbonate disposal strategies. The second strategy is the injection of carbonate or bicarbonate brines into underground reservoirs. A third option is to form solid carbonates that can be stored either on the surface or underground. These solids may be soluble in water and would have to be stored in salt caverns, or they are insoluble and could be stored on the ocean floor or on the terrestrial surface.

In all cases, sequestration must provide base ions to neutralize the carbonic acid that is subject to disposal. The obvious base ions to be found in nature are alkali or alkaline earth ions. The most common are monovalent sodium and potassium, or divalent calcium and magnesium ions. Other carbonate-forming elements are either too rare or too valuable (50, 51). For example, in forming iron carbonates one consumes valuable iron ore.

However, not all magnesium- and calcium-bearing compounds provide alkalinity. For example, rock salt, NaCl, is not a source of alkalinity, as it balances sodium ions with chloride ions. Alkalinity is derived from soluble oxides or hydroxides. These can be extracted from many alkali and alkaline earth silicates or from salts of other weak acids. In disposing of carbon dioxide in the form of bicarbonate salts, one can even use naturally occurring carbonates as a ready, inexhaustible source of alkaline ions. Rau & Caldeira (52) proposed the following reaction for carbon dioxide disposal,

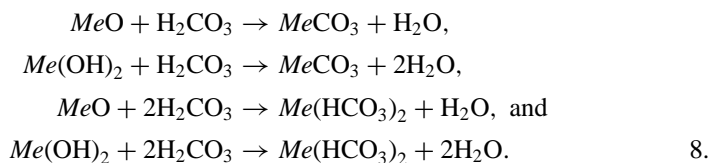


Calcium and magnesium carbonates are found all over the world. Even sodium carbonate deposits exist in quantities sufficient to arouse economic interest. Trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) deposits in Wyoming and Colorado exceed 100 billion tons (53). Because sodium carbonate is water soluble, low cost leaching processes for their extraction make the introduction of mineral sequestration by this route attractive, even though the resource size is not sufficient for full-scale carbon dioxide disposal.

If the disposal product is carbonate brine or solid carbonate, the source of the alkaline ions cannot be a carbonate but is likely a silicate mineral rich in magnesium or calcium. Carbonic acid, being the stronger acid, drives silicic acid out of its salts resulting in carbonates and silica, which is the anhydrous form of silicic acid. Because carbonates are thermodynamically favored, the process occurs naturally in rock weathering (46, 54).

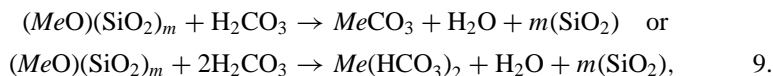
There are plenty of magnesium and calcium silicates, and for some the chemical conversion to carbonate by industrial processes is possible (2). For example, magnesium ions can be extracted from serpentine and olivine rocks (55–58). Peridotite deposits rich in serpentine and olivine exist in many places on all continents. Total estimates are measured in hundreds of thousands of gigatons (50, 59). Basalt, which is rich in calcium, is ubiquitous, but it is more difficult to extract calcium from basalts than it is to extract magnesium from peridotite rock. Not much work has gone into extraction of sodium and potassium from basic minerals, but it is a classical weathering process (4), and many brines are already rich in alkali ions (3). Unfortunately, these brines are most often saline rather than alkaline.

In summary, carbon sequestration requires the neutralization of carbonic acid. The following reactions starting from metal oxides or hydroxides might be considered:



Somewhat arbitrarily we have chosen *Me* as a divalent metal ion, but the translation of these formulas to a monovalent ion such as sodium is straightforward.

The above reactions are only of academic interest because the availability of the appropriate oxides or hydroxides is severely limited. Instead one is likely to start either from the corresponding silicates,



or, if one is willing to forgo the option of forming carbonates, one may start from carbonates and bind a second carbon dioxide by forming a bicarbonate salt in solution,



Table 2 lists some of the common minerals that could be used as sources of alkalinity.

It is far easier to transform carbonates into bicarbonates than it is to drive silicic acid out of its minerals. In forming bicarbonates from silicates one requires only half as much silicate as in forming carbonates. Both observations suggest that bicarbonates represent a more convenient form of sequestration. On the other hand, the formation of solid carbonates allows one to contain the waste carbonates in a specified and well-contained location, whereas bicarbonates readily dissolve in water and thus have to be diluted into the environment. Alternatively, they could be injected at high concentrations into underground reservoirs. On the surface, only the ocean is large enough to accept all the bicarbonate that would be formed. It is far from clear whether the logistics of diluting bicarbonates in the ocean are practical or environmentally acceptable. Also the political obstacle in any form of ocean dumping has to be considered carefully.

After forming carbonates or bicarbonates, it is easy to guarantee disposal on virtually geological times scales. Because of their thermodynamic stability and exothermic formation, it is difficult to release the carbon dioxide. Even though it is possible to drive carbon dioxide out of its carbonate with any strong acid, the energy penalty in supplying such an acid is formidable. Formation of sulfuric acid, even from sulfur-rich coal, proceeds on a scale far smaller than the production of carbon dioxide and is therefore insufficient to free the sequestered carbon dioxide. Because natural carbonate deposits are estimated to be on the order of 90 million gigatons, the environmental risk of acids dissolving surface carbonates is not substantially increased by the additional carbonate from fossil fuel consumption.

Thermodynamic stability eliminates the possibility of sudden carbon dioxide releases, which could be hazardous. The limnic eruption of Lake Nyos released the equivalent of one week's output of a gigawatt coal plant and killed 1700 people (60). Stability also eliminates the risk of gradual leaks. Such leaks could cause environmental nightmares through the accumulation of carbon dioxide in the soil and, in inhabited areas, through the accumulation of carbon dioxide in underground structures. Even far smaller leakage rates that would only affect the long-term environmental carbon balance can be ruled out. Thermodynamic

TABLE 2 List of potential minerals for mineral carbonate and bicarbonate sequestration

| Mineral ^a | Chemical formula | Resource size (1000 Gt) | Chemical preprocess | Intermediate product ^b | Direct disposal process | Disposal form ^c |
|----------------------|---|-------------------------|---|---|---|---|
| Sodium carbonate | Na_2CO_3 | $\mathcal{O}(100)$ | None | None | Dissolve in carbonic acid or ocean water | NaHCO_3 |
| Trona | $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ | $\mathcal{O}(100)$ | None/cleaning | Na_2CO_3 | Dissolve in carbonic acid or ocean water | NaHCO_3 |
| Lime | CaO | Synthetic | None | | Dissolve in ocean water, carbonic acid, or carbonate in gas solid reaction with CO_2 | CaCO_3 or $\text{Ca}(\text{HCO}_3)_2$ |
| Limestone | $(\text{Ca}, (\text{Mg}))\text{CO}_3$ | 90 million | Dissolution in bicarbonate or calcination to lime | $\text{CaO}, \text{Ca}(\text{OH})_2$ | Dissolve in carbonic acid | $\text{Ca}(\text{HCO}_3)_2$ |
| Calcite | CaCO_3 | | Dissolution in bicarbonate or calcination to lime | | Dissolve in carbonic acid | $\text{Ca}(\text{HCO}_3)_2$ |
| Aragonite | CaCO_3 | | Dissolution in bicarbonate or calcination to lime | $\text{CaO}, \text{Ca}(\text{OH})_2$ | Dissolve in carbonic acid | $\text{Ca}(\text{HCO}_3)_2$ |
| Dolomite | $\text{MgCa}(\text{CO}_3)_2$ | | Dissolution in bicarbonate, calcination to magnesia lime, or none | $\text{MgO} + \text{CaCO}_3, \text{MgOCaO}$ | Dissolve in carbonic acid or partially in ocean water | $\text{Mg}(\text{HCO}_3)_2$ and $\text{Ca}(\text{HCO}_3)_2$ |
| Dolomitic lime | MgOCaO | Synthetic | | | Dissolve in carbonic acid or in ocean water | $\text{Mg}(\text{HCO}_3)_2$ and $\text{Ca}(\text{HCO}_3)_2$ |

| | | | | |
|---------------------|--|---|---|--|
| Magnesite | MgCO ₃ | None | Dissolve in carbonic acid or ocean water | Mg(HCO ₃) ₂ |
| Dawsonite | NaAl(OH) ₂ CO ₃ | Extract sodium carbonate | Dissolve in carbonic acid or ocean water | Na(HCO ₃) |
| Eitelite | Na ₂ CO ₃ · MgCO ₃ | Cleaning | Dissolve in carbonic acid or ocean water | Na(HCO ₃) + Mg(HCO ₃) ₂ |
| Shortite | Na ₂ CO ₃ · 2CaCO ₃ | Cleaning | Dissolve in carbonic acid or ocean water | Na(HCO ₃) + Ca(HCO ₃) ₂ |
| Basalt | Very large | Leaching may also result in intermediate minerals such as Dawsonite | Slow processes in ocean water | Carbonates/bicarbonates |
| Magnesium hydroxide | Mg(OH) ₂ | Synthetic (but see brucite) | Dissolution in ocean water, direct gas solid carbonation, dissolution in carbonic acid or bicarbonate solutions | MgCO ₃ or Mg(HCO ₃) ₂ |
| Brucite | Mg(OH) ₂ | Small | See magnesium hydroxide | MgCO ₃ or Mg(HCO ₃) ₂ |
| Calcium hydroxide | Ca(OH) ₂ | Synthetic | Dissolution in carbonic acid and slow dissolution in ocean water | CaCO ₃ or Ca(HCO ₃) ₂ |
| Periclase | MgO | Small | Dissolution in carbonic acid from fine powders | MgCO ₃ or Mg(HCO ₃) ₂ |
| Wollastonite | CaSiO ₃ | Small | Dissolution in carbonic acid | CaCO ₃ or Ca(HCO ₃) ₂ |

(Continued)

TABLE 2 (Continued)

| Mineral ^a | Chemical formula | Resource size (1000 Gt) | Chemical preprocess | Intermediate product ^b | Direct disposal process | Disposal form ^c |
|----------------------|--|-------------------------|---|---|--|---|
| Peridotite | Mixture of serpentine olivine and other mafic minerals | $\mathcal{O}(100,000)$ | Extraction of MgO, Mg(OH) ₂ or MgCO ₃ | Mg(OH) ₂ , MgCO ₃ , MgO | See components below | MgCO ₃ or Mg(HCO ₃) ₂ |
| Serpentine | Mg ₃ Si ₂ O ₅ (OH) ₄ | $\mathcal{O}(100,000)$ | Dissolution in HCl, carbonic acid, or other acids leading to MgCO ₃ , Mg(OH) ₂ , or MgO | Mg(OH) ₂ , MgCO ₃ , MgO | Dissolution | MgCO ₃ or Mg(HCO ₃) ₂ |
| Olivine | (Mg,Fe) ₂ SiO ₄ | $\mathcal{O}(100,000)$ | Dissolution in HCl, carbonic acid or other acids leading to MgCO ₃ , Mg(OH) ₂ , or MgO | Mg(OH) ₂ , MgCO ₃ , MgO | Direct carbonation in carbonic acid at elevated temperatures and pressures | MgCO ₃ or Mg(HCO ₃) ₂ |
| Forsterite | Mg ₂ SiO ₄ | Pure deposits are small | Dissolution in HCl, carbonic acid or other acids leading to MgCO ₃ , Mg(OH) ₂ , or MgO | Mg(OH) ₂ , MgCO ₃ , MgO | Direct carbonation in carbonic acid | MgCO ₃ or Mg(HCO ₃) ₂ |
| Potassium feldspar | KAlSi ₃ O ₈ | Very large | Dissolution in water or brine | KOH, K ₂ CO ₃ | Injection into brines | KHCO ₃ or K ₂ CO ₃ |
| Sodium feldspar | NaAlSi ₃ O ₈ | Very large | Extraction of sodium alkalinity | NaOH, Na ₂ CO ₃ | Injection into brines or dissolution of sodium carbonate into the ocean | Na ₂ CO ₃ or NaHCO ₃ |

^aCarbonate minerals can neutralize carbonic acid while turning into bicarbonate salts. The minerals that do not contain carbonate groups can form carbonates as well as bicarbonates in the sequestration process.

^bIntermediate products might result from a processing step that leads to a material that is more readily carbonated. This step would take one to another line in the table.

^cThe end products are materials ready for carbonate or bicarbonate disposal, which can be directly generated from the input materials.

stability eliminates the need for long-term monitoring and continued maintenance of the disposal site.

OCEAN DISPOSAL

If carbon dioxide is accompanied by the appropriate amount of sodium or calcium ions, the ocean could absorb far more than the next century's carbon emissions (52, 61, 62). One might combine carbonic acid with hydroxides of sodium or calcium and add the appropriate mixture of carbonate and bicarbonate salts to the water. It is also possible to add a pure base, i.e., magnesium, sodium, or calcium oxide or hydroxide, and let the atmosphere-ocean gas exchange pull carbon dioxide directly from the air. This would eliminate the need for carbon capture at the source. In either case, adding alkalinity to the ocean makes it possible to control the carbonate ion concentration or the pH of the ocean water. Indeed it has been pointed out by Kheshgi (61) that adding alkalinity to the surface ocean may need to be considered simply to compensate for the acidification of oceanic surface waters caused by the rise in the atmospheric carbon dioxide concentration.

The Role of Alkalinity

Adjusting the alkalinity adds a new degree of freedom to managing ocean water chemistry and atmospheric carbon dioxide concentrations. With this new option, several different strategies could be pursued. By adding alkalinity to the surface water, one could maintain a constant P_{CO_2} over the water. This strategy would minimize greenhouse gas impacts by effectively removing excess carbon dioxide from the air. Alternatively, over long timescales one could aim for constant pH or constant carbonate concentration. These strategies would each minimize certain impacts on the aqueous chemistry in surface waters.

Tables 1, 3, and 4 lay out the relationship between the various parameters describing ocean water. For simplification in an analysis looking for overall trends, the small contributions of $[\text{CO}_2]$, $[\text{OH}^-]$ and $[\text{H}^+]$ to the alkalinity A and the total dissolved carbon C have been ignored. Also, the effect of borate buffering in ocean water has been neglected. Table 3 lists the functional forms of C , P_{CO_2} , $[\text{CO}_3^{--}]$, $[\text{HCO}_3^-]$, and $[\text{H}^+]$ in terms of different independent variables. For carbon management applications, the most important independent variable is A because it very directly controls the amount of stored inorganic carbon. P_{CO_2} , $[\text{H}^+]$ or $[\text{CO}_3^{--}]$ are natural choices for the second independent variable. P_{CO_2} is driven by fossil fuel consumption and ocean uptake. One may want to control its value by titrating ocean water with alkalinity, i.e., sodium carbonate. Alternatively one may want to manage the pH or the carbonate ion concentration, which impacts water chemistry and ecology. By holding one of these three variables constant, the dependence of the other two as a function of alkalinity is prescribed.

The following identity, which reflects the equilibrium between gaseous and dissolved CO_2 and the first and second disassociation constants of carbonic acid,

TABLE 3 Approximate relationships between parameters describing ocean water carbonate chemistry

| | C^a | P^c | $[\text{CO}_3^{2-}]$ | $[\text{H}^+]$ | $[\text{HCO}_3^-]$ |
|--------------------------------|---|--|--|--|-----------------------------------|
| $C(A, P)^{\text{a,b,c,d}}$ | $A \frac{P+3A}{P+4A} = A \frac{1+3\gamma}{1+4\gamma}$ | P | $A \frac{\gamma}{1+4\gamma}$ | $K_2 \frac{1+2\gamma}{\gamma}$ | $A \frac{1+2\gamma}{1+4\gamma}$ |
| $C(A_0, P)^e$ | $A_0 \frac{P+3A_0}{P+4A_0} = A_0 \frac{1+3\gamma}{1+4\gamma}$ | P | $\frac{P_0}{P} A_0 \gamma_0$ | $K_2 \frac{P+2A_0}{A_0}$ | $A_0 \frac{1+2\gamma}{1+4\gamma}$ |
| $C(A, P_0)^e$ | $A \frac{kP_0+3A}{kP_0+4A} = A \frac{1+3\gamma}{1+4\gamma}$ | P_0 | $\frac{A^2}{A_0} \frac{\gamma_0}{1+4\gamma}$ | $K_2 \frac{P_0+2A}{A}$ | $A \frac{1+2\gamma}{1+4\gamma}$ |
| $C(A, [\text{CO}_3^{2-}]_0)^e$ | $A - A_0 \varepsilon_0$ | $\frac{(A-2A_0\varepsilon_0)^2}{A_0\varepsilon_0}$ | $A_0 \varepsilon_0$ | $K_2 \frac{A-2A_0\varepsilon_0}{A_0\varepsilon_0}$ | $A - 2A_0\varepsilon_0$ |
| $C(A, [\text{H}^+]_0)^e$ | $A(1-\varepsilon_0)$ | $A \frac{P_0}{A_0}$ | $A \varepsilon_0^f$ | $K_2 \frac{P_0+2A_0}{A_0}$ | $A(1-2\varepsilon_0)$ |

^aThe inorganic carbon chemistry of seawater relevant to engineering additional carbon uptake is well known but usually not organized from this point of view. For carbon sequestration the primary function to consider is the total dissolved inorganic carbon C .

^b C is a function of two independent parameters. In all cases we consider A as the first independent variable. The alkalinity A needs to be controlled if one is to allow the ocean to take up substantial amounts of additional carbon. For the second parameter, there are many different choices. For carbon management one natural choice is P , which is driven by fossil fuel consumption. The current uncontrolled experiment (63) of global climate change is proceeding at constant A and increasing P .

^c P is controlled by the emissions of carbon dioxide into the atmosphere; unless alkalinity injections are large enough to change P . Strategies of titration may aim at holding P , the carbonate ion concentration, or the pH constant. For that reason, we tabulate all expressions with each of these three parameters as the second independent variable.

^dThe dimensionless variables γ and ε are introduced because for typical seawater composition they represent naturally small parameters that can be used in a perturbative expansion. To simplify the expressions, higher order terms in these quantities have been ignored. Because of these assumptions, the equations only apply in the vicinity of standard seawater composition. At extreme changes in A or P/CO_2 , the approximations break down because H^+ or OH^- concentrations may no longer be ignored.

^eParameters subscripted by zero, e.g., A_0 , refer to a fixed state, specifically the standard state of seawater. The tabulated formulas result from a simple expansion around standard seawater. In the alkalinity and total dissolved carbon, the dissolved CO_2 , OH^- , and H^+ concentrations are neglected. Near the composition of seawater, this approximation is justified.

^fAt constant pH, the ratio of carbonate ions to bicarbonate ions is constant. Therefore $\varepsilon = \varepsilon_0$, and the carbonate concentration is simply linear in A .

is at the heart of all of these relationships;

$$K_H P_{\text{CO}_2} = [\text{CO}_2] = \frac{[\text{H}^+][\text{HCO}_3^-]}{K_1} = \frac{K_2 [\text{HCO}_3^-]^2}{K_1 [\text{CO}_3^{--}]}. \quad 11.$$

With the approximations of $A = [\text{HCO}_3^-] + 2[\text{CO}_3^{--}]$, $C = [\text{HCO}_3^-] + [\text{CO}_3^{--}]$, and the shorthand notation of $P = \frac{K_1}{K_2} K_H P_{\text{CO}_2}$ the last relation becomes,

$$P = \frac{(2C - A)^2}{A - C}. \quad 12.$$

This equation can now be manipulated to obtain C as function of A and P . In the spirit of the above approximations, one can make use of the fact that for seawater $|A - C| \ll |A|$ and $P \gg A$. This allows expansions in terms of $\varepsilon = (A - C)/A$ and $\gamma = A/P$;

$$C(A, P) = A \frac{1 + 3\gamma}{1 + 4\gamma}. \quad 13.$$

Similarly, one can express $[\text{H}^+]$ and $[\text{CO}_3^{--}]$ as functions of C and A and invert to obtain C as function of A and $[\text{CO}_3^{--}]$, or A and $[\text{H}^+]$,

$$C(A, [\text{CO}_3^{--}]) = A - [\text{CO}_3^{--}]; \quad C(A, [\text{H}^+]) = A \frac{[\text{H}^+] + K_2}{[\text{H}^+] + 2K_2}. \quad 14.$$

Again, one can make use of the fact that $[\text{H}^+] \gg K_2$. See Table 1 for definitions and values of the second disassociation constant K_2 . Because pH, carbonate ion, and bicarbonate ion concentrations are simple functions of C and A , it is straightforward to express these variables as functions of the chosen dynamic variables.

These simple formulas are not a substitute for more detailed models (15, 45, 49) but are only meant to provide a first look at the overall trends. Based on these simple formulas one can estimate the response of ocean water chemistry to changes in the alkalinity, the partial pressure of CO_2 , and the resulting changes in pH, carbonate, or bicarbonate concentrations (Table 3). Note that these formulas make use of numerical relations between variables in seawater and thus cannot be generalized to different water sources or brines.

According to Table 3, changes in P_{CO_2} at constant alkalinity cause equally large relative changes in H^+ and CO_3^{--} concentrations, but bicarbonate concentrations and total dissolved carbon change relatively little. By adding alkalinity one moves the impact onto the far larger reservoir of bicarbonate ions. After adding alkalinity, bicarbonate ion concentration and total carbon concentration change by roughly equal amounts. As a result the relative change in carbonate ion and proton concentrations is far reduced. Cation concentrations, such as those of sodium or calcium ions, are already very large and thus are hardly affected by these changes.

To summarize these trends, Table 4 lists the logarithmic derivatives of C with respect to A , P_{CO_2} , $[\text{CO}_3^{--}]$, and $[\text{H}^+]$. These derivatives are similar in nature to the Revelle factor. Indeed the first entry $\partial \ln C / \partial \ln P|_A$ is the inverse of the Revelle factor. The small value of $\partial \ln C / \partial \ln P|_A$ indicates that for constant A

TABLE 4 Partial logarithmic derivatives of the total dissolved inorganic carbon C . For definitions see Table 1

$$\begin{array}{l}
 (a) \quad \left. \frac{\partial \ln C}{\partial \ln P} \right|_{A=\text{const}} = \frac{\varepsilon}{1+3\varepsilon}, \\
 (b) \quad \left. \frac{\partial \ln C}{\partial \ln A} \right|_{P=\text{const}} = 1 - \frac{\gamma}{(3+\gamma)(4+\gamma)}, \\
 \quad \quad \left. \frac{\partial \ln C}{\partial \ln A} \right|_{[\text{CO}_3^{--}]=\text{const}} = \frac{A}{C} = \frac{A}{A-A_0\varepsilon_0}; \quad \left. \frac{\partial C}{\partial A} \right|_{[\text{CO}_3^{--}]=\text{const}} = 1 \\
 \quad \quad \left. \frac{\partial \ln C}{\partial \ln A} \right|_{[\text{H}^+]=\text{const}} = 1
 \end{array}$$

(a) The logarithmic derivative relates the relative change in the dependent variable to that in the independent variable. The logarithmic derivative of C relative to P at constant A is the inverse of the Revelle factor. Due to the approximation made here, it is monotonic. A full calculation would show that the Revelle factor at large P turns around once the buffering capacity of the carbonate/bicarbonate system has been exhausted. If the alkalinity is held constant, the logarithmic derivative with respect to P is small, i.e., large changes in partial pressure will only lead to small relative changes in the total dissolved carbon concentration.

(b) For changes in the alkalinity, the logarithmic derivative is approximately 1, regardless of which other parameter is held constant. Thus changes in total dissolved carbon are approximately proportional to changes in the alkalinity.

the response of the total dissolved carbon to changes in partial pressure is small. In contrast, C is nearly proportional to A with a proportionality factor close to 1, whether the second independent variable is P_{CO_2} , $[\text{H}^+]$ or $[\text{CO}_3^{--}]$. The deviations from simple proportionality vanish at constant $[\text{H}^+]$. Holding P_{CO_2} constant makes the carbonate ion concentration proportional to the square of the alkalinity. For constant carbonate concentration, P_{CO_2} changes like the square of the alkalinity.

This discussion is reminiscent of thermodynamics. The relevant dynamic variables are all functions of two parameters, and how they change as a function of one variable depends on which second variable is held constant. For example, the enthalpy at constant pressure has a different dependence on temperature than the energy density at constant volume. Here, the carbonate ion concentration is inversely proportional to P at constant alkalinity, whereas it is proportional to P at constant pH. The choices of independent variables made here may not be typical for ocean chemistry applications, but they are most natural in the context of managing carbon in the atmosphere-ocean system.

Changing the alkalinity would raise the uptake capacity of the surface ocean and ultimately of the full ocean. Any carbon management strategy that is based on increasing alkalinity could have the ocean take up 10,000 Gt of carbon with changes in P_{CO_2} , $[\text{CO}_3^{--}]$ and $[\text{H}^+]$ that could be held below 25%. It is remarkable that these changes, which could accommodate the disposal of most of the available

fossil carbon, are smaller than those that have already occurred in surface waters due the increase in P_{CO_2} . At constant alkalinity, the 33% increase in P_{CO_2} that has already occurred has caused a drop of 20% in $[\text{CO}_3^{2-}]$ and an increase of 27% in $[\text{H}^+]$.

A major issue in the biogeochemistry of ocean water is the carbonate ion concentration. At the surface, the ion product $\Omega = [\text{Ca}^{++}][\text{CO}_3^{2-}]$ exceeds the solubility product, even accounting for reduced activities due to the formation of complexes such as $(\text{CaSO}_4)^0$ and $(\text{CaHCO}_3)^+$ (15). Apparently there are kinetic barriers to forming pure calcite or aragonite crystals, and ions attached to actual rather than ideal surfaces are in an energetically higher state. The simplest analog is the elevation of water vapor pressure over the surface of small droplets, which leads to a substantial supersaturation before steam condenses out as liquid droplets. The solubility product has proven important in the biogeochemistry of aragonite formation in coral reefs; it is likely that human-caused excursions in this quantity should be limited. Increases in the alkalinity offer the possibility of minimizing changes in the carbonate ion concentration.

Controlling the alkalinity of the ocean may be motivated not so much by a desire to eliminate the climate change impact of fossil fuel consumption but by the desire to correct the chemical imbalances caused by the dissolution of carbonic acid in the world's oceans. As a by-product of maintaining the oceans' carbonate ion concentration and pH as close to constant as possible, the increased carbon uptake capacity of the oceans would remove nearly all the excess carbon dioxide from the atmosphere and retain it on geological timescales.

The rate of carbon dioxide uptake into the oceans would be limited by the speed of the overall water circulation. Uptake times would be comparable to the time it would take the entire ocean to equilibrate with a change in atmospheric carbon dioxide concentrations without changes in alkalinity. In short, the oceans would still require on the order of a thousand years to allow for 10,000 Gt of carbon dioxide disposal. On the other hand, because a large fraction of the water mixes on shorter timescales (46), this input curve will be biased towards earlier times, which would fit well with a carbon era that for other reasons will run its course in a matter of a few hundred years.

Injecting Alkalinity at the Ocean Surface

Lime stone, dolomite, and trona all provide large sources of alkalinity that could be brought in from continents and injected into the surface ocean. Though it would be possible to use alkalinity extracted from silicate minerals, this would require more expensive preprocessing in order to prepare the input material. However, the same amount of cations would bind twice as much carbon dioxide.

Dispersal of alkalinity would require the transportation of alkaline materials on a scale five to ten times larger than today's fossil fuel transportation. This implies a substantial cost; but unless the injection process is technically very involved, the cost of distributing alkalinity should still be small relative to current energy costs.

After all, transportation costs do not dominate energy costs, and ocean transport in particular is low in cost.

Injecting alkalinity in the ocean poses the technological challenge of maintaining all ions in solution at the injection point. Large changes in pH, calcium ion concentration, magnesium ion concentration, or carbonate ion concentration even if localized could lead to the local precipitation of carbonates or hydroxides, which would remove alkalinity from the water. Calcium carbonate once precipitated would not redissolve, as the water is already supersaturated.

Injecting carbonates rather than hydroxides into ocean waters would avoid large pH spikes but it still could lead to local precipitation because it would raise the carbonate ion concentration, potentially by very large factors. The rapid dissolution of sodium carbonate would likely be prone to such difficulties and most likely would require a careful injection design. The naturally slow dissolution of magnesium carbonate may prove adequate, but calcium carbonate would not dissolve at all, as seawater is already supersaturated.

Another approach might be to prepare bicarbonate solutions under a high carbon dioxide atmosphere and directly inject the solution into the ocean. Unfortunately, unless they are introduced at a depth at which pressures exceed the P_{CO_2} of the concentrated bicarbonate solution, during dilution such a solution crosses a parameter regime in which calcium carbonate is likely to precipitate. Rau & Caldeira (52) avoid this problem by providing a very dilute calcium bicarbonate solution that can enter the ocean without forming precipitates.

Another, somewhat counterintuitive, approach would be to calcine dolomite and introduce the alkalinity either as oxides or hydroxides into the ocean. The material would need to be dispersed, and the rate of dissolution would have to be limited so that local excursions in calcium concentrations or pH do not cause carbonate precipitation. However, the background Ca^{++} concentration is so high that excursions in this quantity are relatively easy to contain. For each mole of magnesium or calcium two moles of CO_2 would be absorbed from the air. This would more than compensate for the upstream release of carbon dioxide, which in any case could have been captured and disposed of underground.

Introducing Alkalinity at the Ocean Floor

Calcareous oozes at the ocean floors, particularly the Atlantic, could prove to be a ready source of vast amounts of alkalinity that might be brought in contact with large volumes of concentrated carbon dioxide that is injected into the deep ocean. By forming bicarbonates, one could stabilize the injected carbon dioxide. This approach to carbon dioxide disposal in the deep ocean would effectively eliminate the environmental issues related to plumes of acidic water leaving the disposal site and furthermore assure that the carbon dioxide would not be released at the surface on timescales of the turnover of the ocean. Although this approach to carbon sequestration probably requires technological advances in manipulating

carbon dioxide liquid on the ocean floor, Broecker & Takahashi have postulated the same mechanism for the eventual removal of fossil carbon from the surface pool. Carbon dioxide-laden waters naturally subducted to the bottom of the ocean would elevate the lysocline and digest calcites and aragonite sediments. The resulting bicarbonates would be retained in the ocean even after the water has recirculated to the surface (29). The total neutralization capacity of this process is limited to a few thousand gigatons because the sediments also contain a small portion of silicate minerals or clays. As the carbonates are dissolved, the clays remain behind and form a barrier against further dissolution of carbonates.

Precipitating Carbonates with Excess Alkalinity

Whereas dissolving calcium carbonate raises alkalinity, its precipitation removes alkalinity. Precipitation of calcium carbonate raises P_{CO_2} by converting HCO_3^- to CO_2 . Consequently the formation of coral reefs releases rather than sequesters carbon dioxide. However, stimulating the precipitation of calcite, aragonite, or dolomite is net carbon sequestration if one supplies alkalinity from external sources. Carbonate precipitation could proceed in specifically designed ponds or basins and could remove carbon dioxide without net changes to the water chemistry. It would, however, require a source of alkalinity different from carbonate minerals. An interesting variation on this theme could be based on biological processes that digest alkaline rock, e.g., serpentine, and cause the precipitation of carbonates with carbon dioxide from the air (R. Mehlhorn, private communication).

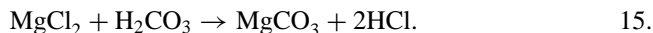
Generally, these approaches to carbon sequestration have not been well explored, and many open questions remain. Although the immediate changes to the water chemistry appear benign, in particular if the alkalinity is sufficiently diluted, one will have to be concerned with the impurities that might be codissolved. Furthermore these geo-engineering options set in motion a dynamical system, which leads to a chain of events that will play out over several millennia. One needs to make sure that the system is stable and that it does not require activities such as continued emissions of carbon dioxide or injections of alkalinity in order to keep it in balance. Mechanisms might involve long-term changes in the depth of the lysocline, which in turn affects the rate at which calcium is recycled from the bottom of the ocean back to its surface. Given the scale of these engineering endeavors, one needs to demonstrate a clear understanding of the dynamics before moving on to a full-scale implementation.

CARBONATE CHEMISTRY IN UNDERGROUND INJECTION

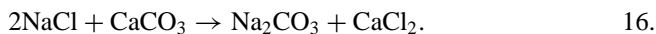
The formation of bicarbonates with imported alkaline materials, the formation of bicarbonates from carbonates residing at the bottom of the ocean, and the precipitation of carbonates with imported alkaline materials all have their analogs in underground disposal. What is different is the concentration of alkaline elements

in the brine, the close contact of the brine with surrounding minerals, and the far lower mobility of pore space fluids relative to that of ocean water.

The first concepts of carbonate disposal started with carbonating alkaline brines from deep underground saline aquifers or magnesium chloride-rich aquifers. Dunsmore considered that a variation of the Solvay process could form carbonates from chlorides, which leave behind hydrochloric acid (3),



The sum reaction of the original Solvay process exchanges carbonate ions and chloride ions between sodium and calcium,



Rather than adding alkalinity, Dunsmore proposed removing acidity, which then would require alkaline materials on the surface or elsewhere underground to neutralize the acid produced.

Carbon dioxide disposal underground has been studied by a number of investigators; see Holloway for a recent review (36). The possibility that reactions with the available mineral matrix could lead to a neutralization of the carbonic acid has long been recognized and under certain circumstances has been viewed as an additional benefit. Most of the early work on this so-called mineral trapping has been discussed and reviewed by the Alberta Research Center (64). The approach follows the basic idea of underground injection of carbon dioxide into deep saline aquifers, but it is the carbonate chemistry that makes it possible to avoid long term monitoring of the well. Some brines are naturally very alkaline and thus could hold large amounts of carbon dioxide. In other situations, acidic bicarbonate solutions could leach additional minerals from the host rock and thus gradually neutralize themselves.

This leaching phenomenon though desirable in some cases, may be undesirable in other circumstances. Acidic, pressurized brines are capable of dissolving minerals and thus increase pore volume. This can drastically change the permeability of the host rock and lead to greatly enhanced mobility of pore fluid. Leaching could even breach the flow barriers on which sequestration relies. On the other hand, carbonate chemistry opens the door to reservoir engineering that, particularly in the case of carbonate rich reservoirs, could shape the behavior of the reservoir. For example, one may consider the possibility of creating high permeability passages in limestone reservoirs near the injection point, where the system is naturally flow limited. As the carbonic acid is neutralized and picks up additional alkalinity in the far field, calcites are likely to precipitate out again and seal up the reservoir.

Leaching also leads to the mobilization of heavy metals. Acidic brines are far more efficient in leaching heavy metals out of mineral rock than alkaline brines and could therefore pose a long-term risk of transporting heavy metals to freshwater aquifers closer to the surface.

Introduction of neutral carbonate solutions into deep aquifers again would reduce the potential for carbon dioxide returning to the surface and for unwanted

dissolutions to occur. It would assure the absence of gaseous carbon dioxide pockets and thus would enhance the long-term predictability of the reservoir.

Even in a reservoir with little opportunity for carbonate chemistry to occur, it may be worthwhile to consider chemical reactions in the overlying cap rock that seals the reservoir. If excess pressure were to open crevices into the overlying rock, the formation of carbonates from the escaping fluids could eventually seal these gaps again. Natural formations of carbonate veins in serpentine rocks are produced by mechanisms similar to those described here (65).

The safety of underground reservoirs and their long-term stability are greatly enhanced by forming mineral carbonates, be they dissolved in the water or solid. One may be able to show that in a matter of decades a carbon dioxide filled reservoir is gradually forming carbonates. At this point remnant carbon dioxide may be removed from the reservoir to assure its long-term stability without continued monitoring.

SOLID CARBONATE DISPOSAL

Solid disposal confines the environmental impact to the smallest possible region. As a result local transformations are substantial even if they are relatively benign. Unlike for dilution based disposal, one cannot begin to store solid carbonates without considering the huge volumes of carbon dioxide involved. Solid carbonate disposal is attractive because of its finality. Carbonate is formed in a controlled process and disposed of in a well-defined and specifically chosen site. One does not have to take recourse to complex transport models to be convinced of the safety of the deposit. In this sense, above ground, industrial formation of mineral carbonates best addresses environmental and safety concerns.

Natural resource availability suggests the formation of calcium and magnesium carbonates as the most likely approach. They are difficult to dissolve and to the extent that they are soluble, they form bicarbonates that would bind even more carbon dioxide. Small-scale leaching would therefore be of minor consequence.

Calcium- and magnesium-based carbonates are already plentiful in nature. The natural minerals that precipitated from ancient seas point to the environmental safety of carbonate disposal. However, this line of reasoning must be used with care: Trace elements present in human-made carbonates for disposal would differ from those found in natural materials. Future investigations will have to demonstrate the environmental safety of industrially produced carbonates that carry trace elements passed through from the raw materials. Carbonate minerals are slightly alkaline and thus are far more benign than acid mine tailings, which tend to promote the leaching of heavy metal trace elements. Preliminary tests indicate that magnesium carbonates made from serpentine pass simple leaching tests (66).

There are two reasons that favor magnesium ores over calcium ores in solid mineral carbonation. Magnesium silicates tend to be richer in base ions than calcium silicates, and magnesium silicates are usually more reactive than calcium

silicates. Magnesium silicates can be carbonated (57, 67–70). Among the calcium resources, wollastonite has been successfully carbonated at temperatures and pressures relevant for industrial processes (71). Unfortunately, wollastonite resources appear far too small to be of practical interest.

Disposal of sodium carbonate or bicarbonate in salt cavities would be a special case of solid carbonate disposal. Because sodium salts are highly water soluble, they need to be stored at a location that is safe from water intrusion. It would open a new option to mineral sequestration that could rely on sodium rich minerals as the source of alkalinity. At first sight it appears that salt caverns could provide substantial storage space, but in order to provide enough volume these caverns would have to be leached out, leaving behind a major salt disposal problem. Though this disposal process is no larger than the dispersion of alkalinity in the ocean discussed above, unlike alkalinity dispersal it would not address changes in the ocean chemistry.

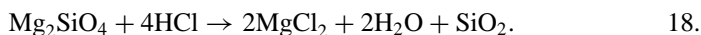
Hydrochloric Acid Process for Magnesium Carbonate Disposal

The observation that olivine and serpentine are readily dissolved in hydrochloric acid (56) has focused much attention on these two minerals. Even though the hydrochloric acid extraction of magnesium at this point does not appear practical, it is of interest for two reasons: First it proves that mineral sequestration is chemically feasible without heat treatment. Second, it is a prototype for other acidic dissolution processes that may be energetically easier to perform.

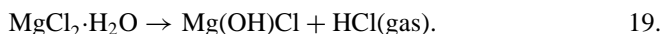
Hydrochloric acid extraction is a straightforward procedure. For serpentine, the acid dissolution reaction is given by



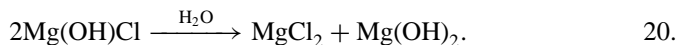
For forsterite, a magnesium olivine that also dissolves in hydrochloric acid, the reaction takes a similar form



Both minerals occur in peridotite rocks. The dissolution in hydrochloric acid is exothermic and self-heating and progresses quite rapidly. Some care needs to be taken to avoid forming silica gels and to manage the dissolution and subsequent precipitation of iron oxides that are always present in serpentine and peridotite rocks. Recipes for these leaching processes exist and have been used in industrial practice (55, 72). The major difficulty lies in recovering the hydrochloric acid. The thermodynamics of the $\text{MgCl}_2\text{-H}_2\text{O-HCl}$ system is well explored and well understood (73–75). At temperatures around 200°C to 230°C, hydrated magnesium chloride is unstable and disassociates into hydrogen chloride and magnesium hydroxy-chloride,

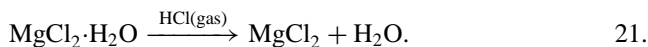


This step recovers half of the HCl. The other half can be recovered by dissolving the mono-hydroxide in water where it disproportionates,



By cycling the MgCl_2 again through this process one closes the HCl recovery loop.

The hydrochloric acid process is closely related to the first stage in Noranda's process for producing magnesium from serpentine. The Noranda process, by maintaining a high HCl pressure over the hydrated chloride melt (76), avoids the formation of magnesium mono-hydroxy-chloride and instead forms anhydrous magnesium chloride that is used in the electrolytic production of magnesium.



Wendt et al. (77) worked out the details of the hydrochloric acid extraction of magnesium from serpentine and olivine and concluded that the energy cost of the associated evaporation of water is too high for an economically viable implementation. Although one should not downplay this problem, it is also easy to exacerbate these losses in a strawman design that is too cavalier about recapturing heat and reaction products. Haywood et al. (78) sketched out a process in which 30% of the HCl is considered irretrievably lost in the form of MgCl_2 , which is mixed in with the product $\text{Mg}(\text{OH})_2$. Even if one were to follow such a process design, this $\text{Mg}(\text{OH})_2$ - MgCl_2 mixture would make an excellent, low-cost source of makeup MgCl_2 , thereby negating the claim that the acid is irretrievably lost. The report by Wendt et al. outlines an explicit approach to recovering this chloride and worked out one implementation that would only impose a 40% energy penalty. Because this process requires only low-grade heat, tight integration with a power plant could lead to a design where the electricity output of the power plant would drop even less.

Molten Salt Extraction

By dissolving the serpentine or olivine directly in an acidic hydrated melt of magnesium chloride one could reduce the amount of water that would need to be evaporated. At low temperatures, magnesium chloride solidifies as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, but at higher temperatures, there can be less water in the melt. At operating temperatures around 200°C , the melt would never require more than one or two moles of water per mole of magnesium chloride, and it would be sufficiently acidic to dissolve serpentine rock. Although the thermodynamics of this dissolution has been computed, the kinetics of the reaction still needs to be determined experimentally (79). Unfortunately the disproportioning of $\text{Mg}(\text{OH})\text{Cl}$ (Equation 20) does not happen unless the mixture has at least six waters per mole of Mg. Therefore, in forming magnesium hydroxide one cannot avoid diluting the reagents in water (77). With all the water present, the inefficiencies in evaporating this water again raise the energy demand. The path to $\text{Mg}(\text{OH})_2$ seems to be blocked. However, thermodynamic calculations suggest that the direct carbonation of molten

Mg(OH)Cl should be feasible. Thus it has been suggested to combine driving off hydrogen chloride and precipitating carbonate into a single step (79).

This approach, which is again very close to a modern implementation of the Noranda process, involves hot, pressurized highly corrosive materials, and easier alternatives are desired. One such approach is the use of less aggressive acids, the most obvious being carbonic acid, but it also includes other alternatives such as acetic (71) and citric acid. A process for extracting MgCO_3 from serpentine tailings with ammonia bisulfate $(\text{NH}_4)(\text{HSO}_4)$ was patented in 1967 (80).

Dissolution of Serpentine and Olivine in Carbonic Acid

It has been known for some time that the dissolution of serpentine in carbonic acid is possible. Drăgulescu et al. demonstrated a process in which magnesium is extracted from heat-treated serpentine by dissolving it in carbonic acid (57). The original purpose of this technique was to develop serpentine ores for magnesium production. This is an environmentally friendly process, which involves neither chlorides nor other aggressive chemicals, but it arrives at pure magnesium carbonate.

Recently a group at the Albany Research Center (70) studied this reaction for mineral carbonate disposal. The initially slow dissolution process has been greatly improved. In the presence of pressurized carbon dioxide and dissolved sodium bicarbonate and sodium chloride, the speed of the process was greatly enhanced. The reaction with serpentine is, however, still too slow unless the material is first heat-treated at about 650°C . That heat treatment activates serpentine has been well known since the 1950s (56). Unfortunately, the penalty of such pretreatment in terms of energy and additional cost is still too high to allow for an economic implementation.

The current implementations are laboratory devices not yet ready for industrial applications, which would need to operate at slower rates of agitation and with less finely milled materials and at lower pressure. The carbonate precipitates are still too fine to allow rapid dewatering, but it would be premature to fine-tune the end stages of the precipitation until the dissolution step has been fully developed.

Other Options

The most difficult challenge still remains the heat treatment step for serpentine. It raises the cost of the process to unacceptable levels. One possible path around it would be to abandon serpentine in favor of olivine. Dunite, pure magnesium olivine, can be carbonated without pretreatment (81, 82). There are large olivine deposits, for example at Twin Peaks, Oregon and in the Oman coastal range. Nevertheless, limiting mineral carbonation to completely unserpentinized dunites would raise costs. It also would put in question the ability of solid mineral sequestration to cope with the full scale of fossil fuel consumption. The goal of reaching this large scale of carbon disposal makes it worthwhile to further explore the serpentine options.

Options indeed exist. Mechanical excitations seem to increase reactivity (83), and recent results from the Albany group confirm that attrition grinding of serpentine leads to extremely high reactivity. Citric acid and EDTA are two chelating agents that have been shown to break serpentine minerals apart (H-J Ziock, private communication). Although none of these approaches is ready for economic implementation, they point toward additional directions for research. A better understanding of the microscopic reaction details could help develop better processes for mineral sequestration. Much progress in this regard comes from the McKelvy group at Arizona State University that is beginning to develop a molecular level model of the reactions involved (85, 86).

COST ISSUES

Although this paper focuses on the chemistry of carbonate sequestration, it cannot avoid discussing the costs of carbonate disposal. Because any carbonate sequestration would have to provide alkalinity, it incurs costs that simple disposal of carbon dioxide would avoid. Whether the alkalinity has been extracted from a mined mineral such as peridotite rock or has been obtained by pumping fluids through a rock formation, one is adding a relatively expensive unit operation to the process of carbon sequestration.

The generic carbonate or bicarbonate disposal process involves several distinct steps, each adding its own cost to the process: extraction, transportation, preprocessing, carbonation, and disposal or dispersal. Not all steps are equally difficult for all processes.

Extraction of Alkalinity From Mineral Reservoirs

This step is common to nearly all carbonation approaches. The one exception is the injection of carbon dioxide underground for in situ reactions. Otherwise one needs mining operations to extract carbonates or silicates—or leaching operations to extract dissolved alkaline minerals.

The cost of creating alkaline brines has not been researched in the context of carbon dioxide disposal, but the cost of mining, crushing, and grinding rock is well known. Costs depend on the size of the mine, the hardness of the rock, and other parameters. For the large-scale operations considered in the context of mineral sequestration, costs are typically a few dollars per ton of rock processed. Mining costs include digging up ore, crushing and milling, disposal of the mine tailings and disposal of the carbonate mineral products. They do not include chemical processing and possibly extensive post-processing steps to put carbonates into a suitable disposal form, e.g., filtration, dewatering, or the cementation of material into larger aggregate. A number of reviews on this topic led to estimates between \$7 and \$15 per ton of CO₂ (81, 82, 87). Larger operations would lead to lower costs.

In order to benefit from economies of scale, mines need to be large—able to process in excess of 100,000 tons of rock per day, which puts them into the

class of the largest mining operations. This scale is necessary, as single units of mining equipment already operate on this scale. For serpentine mining large scale operations are possible because deposits tend to be extensive. At several 100,000 tons of serpentine per day, a single mine would process the carbon dioxide emissions from many gigawatts of electricity generation. To set the scale, a 50% efficient coal-powered plant generating 1 GW would require about 40,000 tons of serpentine per day. A natural gas-powered plant would require roughly half that amount.

Worldwide mining operations would be large but not unprecedented. Aggregate mining today approaches similar numbers, and it is performed in far smaller and therefore far more numerous and more costly operations. A surface coal mine would be larger than the corresponding serpentine mine (88). Overburden mass moved in a coal mine tends to exceed the mass of serpentine required, whereas serpentine mining would not involve significant overburden. Because serpentine mining does not have to follow a thin seam, the area of a serpentine mine would be substantially smaller than the equivalent coal mine.

Mining of limestone or dolomite would lead to comparable costs, whereas leaching processes could be far more cost effective. Comparison for these costs should come from injection of fluids underground and the reprocessing of these fluids.

In estimating the cost of the extraction of alkaline materials, it is important to realize that the scale of mining serpentines for carbonate disposal would be so large that it would drive the environmental regulations, which in turn could inflate mining costs. Serpentine mine operations have to contend with the presence of chrysotile asbestos in the ore (51), which is an environmental concern. A recent unpublished study performed by Nexant Inc. (J. Ruby, private communication), suggests that based on current practice and current regulation this is not a cost driver. However, serpentine mining for carbonate disposal because of its size would have to aim at environmental performance levels that far exceed current regulatory standards.

Transportation

For coal power, overland transportation costs are a significant part of the fuel cost adding about \$7 to \$10 to the cost of a ton of coal. The mass of alkaline materials used to neutralize the resulting carbon dioxide would be far larger. In the case of serpentine, the multiplier is around seven. For other alkaline materials, similar multipliers apply. Limestone has about eight times the weight of the disposed carbon. If at all possible, one would avoid transporting the alkaline materials in favor of the lower mass of carbon or the more mobile carbon dioxide. In cases where this is not possible, expect the transportation cost to be a major contributor to the overall sequestration cost.

Underground injection and disposal of solid carbonates may not require the transport of alkaline materials and thus are less affected by this concern. Ocean disposal options require the shipping of alkalinity or product carbonates that weigh in at two to three times the mass of the carbon dioxide. Fortunately, shipping of

solids on the ocean is very cost effective. The mass transported is comparable to the mass of compressed carbon dioxide that needs to be transported in carbon dioxide injections into the ocean. We therefore consider these cost estimates as upper limits on the cost of alkalinity based disposal.

Preprocessing and Carbonation

Although mining costs are likely below \$10 per ton of CO₂, processing costs for some of these methods could be higher than that. Breaking up silica structures in order to extract the alkaline materials represents a substantial cost. For serpentine carbonation, a recent unpublished study by Nexant Inc. has scaled up the current laboratory implementations and suggested costs in the range of \$70 per ton of CO₂. A dominant cost is the heat treatment step, which also incurs a substantial energy penalty. If this hurdle can be overcome, \$20 to \$30 per ton of CO₂ provide a reasonable cost goal. Independent assessment of these estimates is still required.

Dispersal or Disposal

In the disposal of solid carbonates, we have assumed that disposal is incorporated into the mining operation. However, the volume of the disposal product is bound to exceed the volumes mined. Even without the mass increase due to the binding of carbon dioxide, volumes would increase through lowered packing density. Constraints on managing these excess volumes again could drive long-term costs.

Disposal in the ocean requires some effort in dispersing and diluting the material. The overall effort, however, could be tolerable in cost. If, for example, one insists that even local alkalinity should not change by more than a factor of two, then the rate at which material can be discharged from a ship is limited. For example, assume that a ship drops sodium carbonate into the surface ocean and that this alkalinity is mixed immediately into a 10-meter thick layer. Ten meters may be the typical drop distance before small pellets have dissolved. The rate of discharge is now limited to 2 mmol/kg of water or about 2.1 kg of sodium carbonate per square meter of ocean surface. A ship moving at 10 knots (5 m/s), spreading the carbonate into a 1000 m wide swath would therefore inject 10 tons per second into the ocean. Unloading a 300,000 ton freighter would thus require only eight hours, which is probably a small fraction of the travel time to and from the disposal site.

Even though such a cost for neutralizing carbon dioxide prior to or during the disposal may appear large compared to some of the disposal costs quoted for underground injection or ocean disposal, they would be comparable to or less than the total costs incurred in capturing, transporting, and sequestering carbon dioxide by other means (8). Thus they would not qualitatively change the cost of carbon dioxide sequestration.

The long-term costs of verification, monitoring, and continued assurance of the integrity of the storage system are effectively eliminated in carbonate disposal. Because these are recurring costs, they could be quite substantial even if discounted for present day value.

CONCLUSION

Energy is central to worldwide economic development, but none of the present energy technologies could support a sustainable world economy at a living standard taken for granted in the developed countries. A major challenge to today's engineering community is to develop environmentally acceptable, low cost, and abundant energy resources that can provide the next century's energy demand. Failing to step up to this challenge would create an additional crisis point in a world that has plenty of political and economic instability. With ready energy available, material resource limitations, food, and water shortages can be overcome. Most environmental concerns resulting from the emission of pollutants can also be addressed if energy is plentiful, cheap, and abundant. Safe and permanent carbon sequestration options seem to be among the most promising technologies, as they eliminate the need to phase out fossil fuels.

The large scale of today's fossil fuel consumption and its anticipated growth set the scale of the carbon dioxide sequestration problem. At storage scales in the hundreds of gigatons to teratons, disposal of a gas is fraught with difficulties and hazards. Though these difficulties can be overcome in principle, the cost of doing so becomes larger as storage volumes and required storage times increase. This increase in cost gradually will give the chemical transformation of carbon dioxide into a substance that is more readily stored a sufficient advantage to justify the additional expense.

Carbon dioxide disposal is the disposal of carbonic acid. Thermodynamically this acid is unstable in the environment and will eventually find a way of forming the more stable carbonates or dissolved bicarbonates. In the meantime, the environmental impact is large.

Moving towards a thermodynamic low state for sequestration has two advantages: First, it may be accomplished without energy investment. Second it is permanent because it would require energy to return to chemically more reactive compounds. Because natural carbonation reactions are far too slow to help with the environmental concerns of greenhouse gas emissions, carbon sequestration requires the collection of an alkaline base, the acceleration of the carbonation process in an industrial setting, or the transformation of the alkaline materials into a form that readily reacts with carbon dioxide in the air. Thus, carbon dioxide disposal becomes a challenge to the mining engineer and the chemical engineer.

Closing the carbon cycle requires the development of a new extractive industry to provide the alkaline base. In its scale this industry would exceed the fossil fuel extraction industry. The preferred forms of alkalinity would be hydroxides and oxides of sodium, potassium, calcium, or magnesium. Very few of these minerals exist in nature, but there are plenty of silicates and carbonates. The former can be used to form carbonates or bicarbonates; the latter can be used to form bicarbonates. Carbonates can be dissolved in water or stored as solids. Bicarbonates because they are all water soluble are difficult to store anywhere but in solution.

Dissolved bicarbonate disposal could occur in the open oceans or in the vast reservoir of saline water that fills the pores of underground formations, what David Keith calls the “deep hot ocean.” These injections could occur under continents or even below the “surface” ocean (90). The “surface” oceans are already large enough to sequester neutralized carbon dioxide emissions for the foreseeable future. The ocean could even pull the carbon dioxide directly from the air. This would have the added benefit of eliminating the major cost of capture and transport of carbon dioxide.

One can approach modifying the ocean’s alkalinity as a geo-engineering project (61) with the ambitious goal of maintaining either a constant pH or a constant carbonate concentration in ocean water. For this goal to be achieved, alkalinity seeding would have to happen on a truly global scale. On the other hand, every mole of alkalinity added to the ocean will eventually capture two moles of carbon dioxide. To obtain the benefit of sequestration, it is not necessary to think in geo-engineering terms, but one can approach this problem one ton at a time.

Underground injection into saline aquifers is conceptually very similar to ocean disposal. There are, however, differences as well. At a higher pH, these solutions have a far larger carbon dioxide uptake capacity than seawater, and solution of minerals and precipitation of materials in the pore space could play a major role in the overall process design. Underground injection can store bicarbonates or carbonates as solids or liquids. It can be accomplished by making local modifications to a far larger and far more stable system than the ocean. Therefore, underground disposal poses less long-term concerns than ocean based disposal schemes.

Carbonates can be stored as solids, which confines the environmental impacts to the spatially smallest possible volume. There are no unknowns about the whereabouts of the material. Although these volumes ultimately become very large, the scale is measured in multiples of the volume of Lake Michigan; on a global scale, they are small, which essentially eliminates all but local scale concerns over their disposal. Quite likely, the local availability of disposal sites above ground and underground and the local availability of alkaline base are going to determine whether above ground disposal or underground disposal offer a better choice.

Development of sequestration technologies combined with the development of alternatives to fossil energy would maximize the technological options for an energy infrastructure that is sustainable for centuries. Yet, in order to be successful, technology development must break out of a thinking that is rooted in the megawatt to gigawatt scale and start to focus on the terawatt scale that will be required.

Carbon management could start in earnest today. Indeed it has already started in Norway, where \$50 per ton of carbon dioxide gave an incentive for reducing carbon dioxide emissions. Carbon dioxide capture and carbon dioxide transport are already feasible, and in special circumstances they would add very little cost. For sequestration on the initial scales, practical methods already exist and have been demonstrated in field practice. Carbon dioxide is routinely sequestered in enhanced oil recovery, it can be used in coal bed methane extraction, and it is already disposed

of by injection into deep saline aquifers. Our emphasis on carbonate formation is not to slow down the introduction of carbon sequestration but to complement it with technology that would guarantee long-term viability of sequestration.

Considering that a power plant's operational lifetime exceeds fifty years, knowing that long-term options exist becomes an important policy issue. Extracting alkalinity from minerals and neutralizing the acidic end product of fossil fuel combustion address the full scale of the carbon dioxide disposal problem and may virtually eliminate carbon dioxide emissions as an environmental concern.

ACKNOWLEDGMENT

I gratefully acknowledge David Keith and Robert Socolow for many helpful discussions of the manuscript and Columbia University's Earth Institute for its support of my work.

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