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Sequestration of CO₂

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INTRODUCTION

At present 7.4GT of CO₂ are added to the Earth's atmosphere yearly. This is the principal greenhouse gas (GHG). In 1992 CO₂ accounted for 63.6% of the atmospheric radiative forcing. The sources for this CO₂ are about equally divided between 1) industrial, point source stack gases, 2) mobile machinery and 3) commercial and residential outputs. The US accounts for about 23% of total world CO₂ emissions but it also accounts for almost 28% of all productivity while housing less than 5% of the world population. Due to their extensive use of nuclear energy France and Japan have the lowest per GDP CO₂ pollution in the industrialized world. Western Europe also produces more electricity from nuclear energy than does the US so its *per capita* emission value is also less.

Increase in GHG's is believed to be a principal driver for global climate change (GCC) [DOE, 1999; 2001]. There are two sorts of consequences associated with GCC – those whose results are rather linear and those whose consequences are unpredictable and may even be catastrophic. Predictable events are the demonstrated increases in ground temperature in the Northern Hemisphere and in ocean volume with the attendant sea level rise. Catastrophic events are of two sorts – those that are localized though they may have some larger domain spillover effects and those that are inherently worldwide in scope. One of the more dramatic of the latter could be the diversion of the ocean conveyor system driven by the sudden release of glacier melt. Such an event could occur with relative rapidity, perhaps over a period as short as 50 years [Broecker, 1991]. However dramatic and potentially catastrophic, it is more important to realize the relentless and insidious effects such as ocean volume increase and sea level rise are now and will continue to impose major economic costs, e.g., the cost to elevate sewer plants to prevent seawater reflux.

STRATEGIES FOR GHG REDUCTION

While it is clear that GHGs in general, and release of CO₂ in particular, must be reduced what is not so clear is which strategies to use. At a global level the relationships and choices are illustrated in Figure 1.

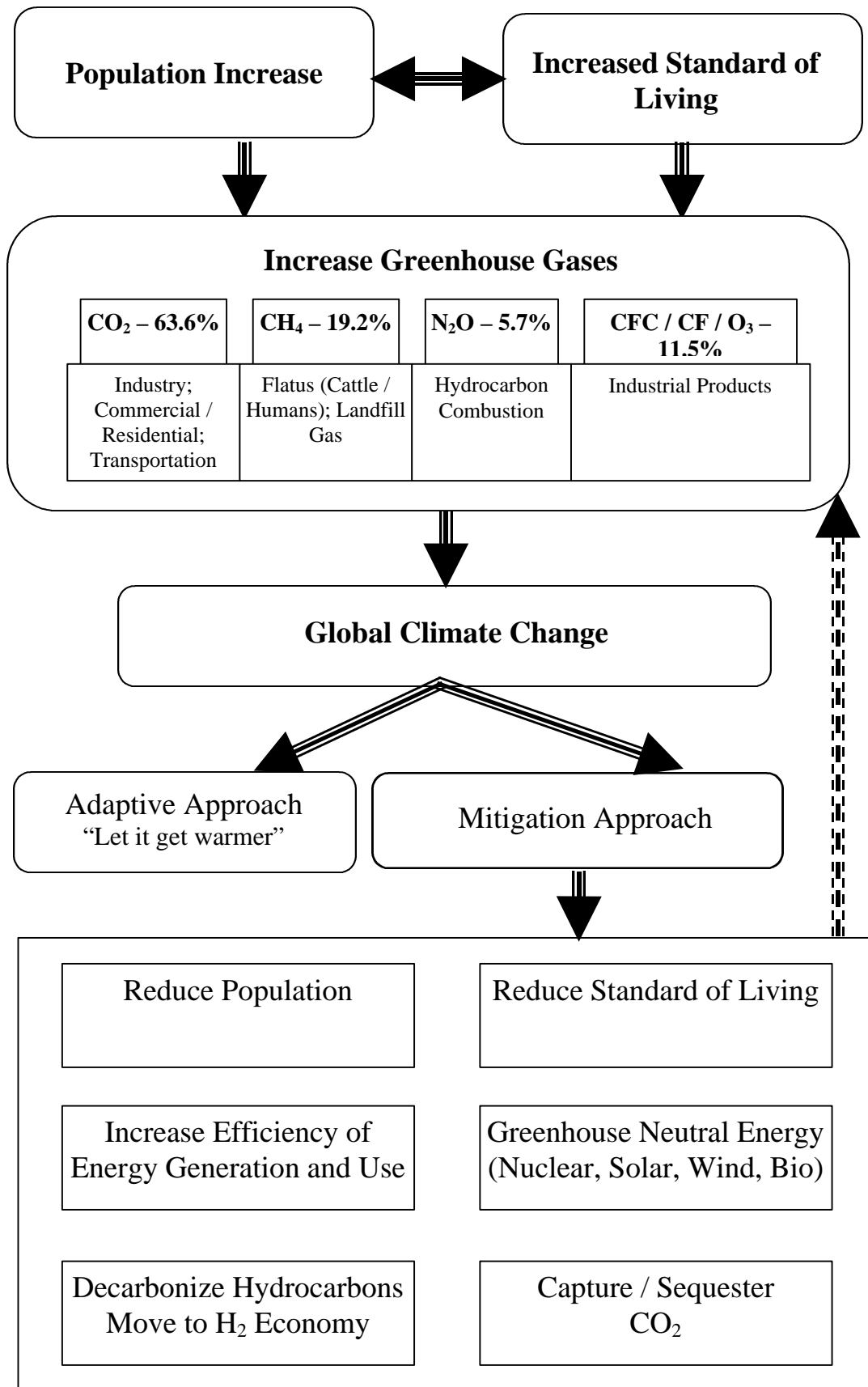


Figure 1. Causes of GHG accumulation and strategies for reducing GHG emissions.

Generally speaking, in the near term, neither population reduction nor decreases or stabilization at current standards of living will be effective drivers. Therefore, we are left with the following options: 1) use less energy by increasing the efficiency of production, distribution and use, 2) utilize greenhouse neutral approaches to produce energy 3) use energy sources that produce less CO₂, and 4) use technology to capture and sequester CO₂. Options 1-5 have in common the theme of making less CO₂ while option 6 alone deals with reducing current and future CO₂ accumulations in the atmosphere without necessarily altering current consumption patterns. All of these approaches can and should be explored though some are more palatable, some easier, others less costly, and yet others more potent, i.e., greater benefit per unit cost and socioeconomic disturbance.

Progress towards viable options is hindered by three classes of operators. The first is the combined effect of the available reserves of hydrocarbon fuels, the installed base of hydrocarbon combustion equipment, the vested interests of hydrocarbon producing, processing, distributing and selling interests. The second is the general lethargy of the political process. The third is the absence of clear and mutually credible paths to efficient, economic growth oriented solutions. The various analyses of the impacts (costs and benefits) of adopting any of the above strategies are so disparate, due to very different initial assumptions, that policy makers can choose the expert opinion that fits their preferred conclusion. Thus, as is commonly the situation with major cultural redirections, we must await one or more significant, if not catastrophic, events as the driver to effective action.

Implementation and utilization of increased energy efficiency are controlled by four major factors – technology, economics, politics and cultural acceptance. Even in the West this approach faces major disincentives from current accounting and market practices as embodied within the political framework. At best 100% implementation might decrease CO₂ emissions by about 15-20%. This assumes a 50% decrease in current electricity transmission losses and a 10-20% improvement in the efficiency of energy use in commercial, residential and industrial settings.

Greenhouse neutral approaches would include both alternate energy production, e.g., wind, solar, hydrothermal, wave, nuclear, and biological approaches, e.g., biofuels. Collectively these might account for CO₂ emission reduction by 6-7%, assuming a 50% increase in electricity generating capacity where all new plants use greenhouse neutral technologies.

Utilization of energy sources that yield less CO₂ essentially means fuel switching, for example from coal to natural gas and from hydrocarbons to decarbonized fuels, i.e., to a hydrogen economy. Decarbonization (in the strict sense of its use) involves processing hydrocarbon fuels before they are oxidized to produce hydrogen and solid carbon. The hydrogen is then used for clean combustion directly or via fuel cells. Perhaps the single biggest technical barrier to introduction of this solution is our current inability to store hydrogen for long periods without significant loss or cost inefficient mass penalties attributable to the storage vessels. Full implementation of a hydrogen economy could have a massive impact on CO₂ emissions, ranging from 66% to 100% but it comes at a significant price in the efficient utilization of energy reserves. The efficiency of hydrogen

generation from natural gas is 59%, from petroleum 25-37% and 19% from coal [Halmann & Steinberg, 1999].

Of all the approaches listed in Figure 1 the one that could have the shortest time to implementation is the capture and sequestration of CO₂. Were the cost of currently available technologies acceptable their use could be initiated today. The US DOE estimates that capture accounts for 3/4 of the combined cost of capture and sequestration. Halmann & Steinberg [1999] have identified a large number of physical, chemical, physicochemical and biological approaches to capturing CO₂. These are summarized in Table 1.

Table 1. A brief listing of CO₂ capture technologies.

- Absorption by liquids
- Strip CO₂ with H₂
- Increased photosynthesis
- Precipitation by carbonates
- Decomposition by low- and high energy radiation
- Acidification followed by degasification
- Dilute phase methanation of atmospheric CO₂
- Adsorption by solids
- Extraction by refrigeration
- Distillation or steam stripping
- Absorption by deep-ocean processes

ABSORPTIVE CAPTURE OF CO₂

Of these alternatives the one that has the greatest experiential base and is closest to implementation, provided that costs could be reduced 2-4-fold is absorption by liquids. For the last 60 years amines and glycol ethers have been used in absorption/stripping tower configurations to capture CO₂ [Astarita et al, 1989]. In the absorption tower, the absorbing rate is controlled by the hydration kinetics of CO₂. In a second tower thermal (steam) swing is used to extract the CO₂ from the CO₂-rich liquid. It is this steam driven step that is cost limiting [Halmann & Steinberg, 1999].

To try to overcome this limitation there have been a number of efforts towards developing an amine-based membrane contactor [Teramoto et al, 1996, 2001]. In one design an amine is immobilized in the pores of membrane (supported liquid membrane – SLM) The other side of the membrane is exposed to a vacuum. The CO₂ partial pressure difference provides the pressure difference that is used to desorb the amine thereby releasing the CO₂. A membrane contactor is essentially a more efficient absorbing tower. While certain laboratory scale reports are very positive [Teramoto et al, 1996, 2001] field used data are considerably less persuasive. In addition some of the amine has been reported to vaporize, passing through the pores of the microporous membrane to contaminate the permeate.

We have approached the problem of how to best capture CO₂ by considering two goals. The first was to develop a system that can operate at ambient temperature and pressure thereby avoiding the thermal cost associated with bulk amine stripping. The second was to create a membrane exhibiting both high permeance and high selectivity while using materials that were environmentally friendly.

We have succeeded at these goals by developing an enzyme-based contained liquid membrane (EBCLM) [Trachtenberg et al, 1999-2002; Ge et al, 2001]. The biological catalyst, enzyme, carbonic anhydrase (CA – EC 4.2.1.1) is used to facilitate the solvation of CO₂ by the rapid conversion of the dissolved gas to bicarbonate. The bicarbonate diffuses across the liquid membrane and reacts with a second quantity of CA at the permeate side gas-liquid interface allowing the CO₂ to evolve into the permeate stream. By means of this design we have dealt with feed streams ranging in CO₂ concentration from about ambient, 0.04%, to values in excess of those found in flue gas, i.e., >20%, specifically as high as 40%. In theory there is no upper concentration limit provided appropriate scaling. To effect this separation we have designed a hollow fiber version of our EBCLM (HF-EBCLM). The design operates independent of humidity levels in the feed or sweep streams and can run for considerable periods of time extracting whatever solvent water is needed from a reservoir. The performance characteristics of this design are such that with a feed of 10% CO₂ the permeance is 2.4×10^{-8} moles/m² s Pa and the selectivity, vs. nitrogen in air is 1800:1.

SEQUESTRATION OPTIONS

It is likely that as the public becomes more knowledgeable about the potential implications of various sequestration options this issue may come to represent a significant fraction of the sociopolitical costs via law suits and NIMBY (not in my backyard) concerns. An event such as the sudden release of CO₂ from an underground storage site could be just such a trigger. There are at least 7 different approaches to disposing of CO₂ [Halmann & Steinberg, 1999]. In addition there are dozens of different candidates for converting CO₂ into simple organic compounds [Halmann & Steinberg, 1999]. In general, technologies for the conversion of CO₂ into usable goods or materials are either at the exploratory stage or early in development. In any case the quantity of CO₂ produced each year via combustion dwarfs the capacity of organic product markets. The better developed of the sequestration options are listed in Table 2. The difficulty, here too, is in choosing amongst these and in making them economically acceptable.

SOLID CARBONATE SEQUESTRATION

Depending on the sequestration option selected the CO₂ would be stored as a gas, a supercritical fluid, a liquid, a solid ice (clathrate) or as a solid salt – metal carbonate. The principal parameters that characterize each of these alternatives are their cost, feasibility, accessibility, safety, risk profile, longevity, prior experience, and state of technical readiness.

We are very experienced in storage of CO₂ as a supercritical fluid as its deposition is used routinely in enhanced oil recovery operations. It is stored for a period of time in a variant known as “huff and puff” before being released. As long as the rock cap does not fracture this is a safe and secure method. Over pressurization is the most important potential problem as it will fracture the overlying rock cap possibly allowing leakage to the surface. Immediate experience with CO₂ storage in salt wells or subterranean aquifers is less well developed though a number of projects are underway exploring aquifer use. Ocean storage has received serious criticism both for its potential damage to marine life and that aside from shore based deposition it will be unacceptably expensive.

Of all these alternatives, and their many variants, one stands out in terms of its potential cost, safety, longevity and prior experience – storage of CO₂ as a solid by the formation of metal carbonates. This process occurs naturally, viz. Weathering and salt formations.

Table 2. A brief summary of sequestration options.

APPROACH	BENEFITS	RISKS / ISSUES	EXPERIENCE LEVEL	REQUIRED CO ₂ PURITY
Underground in abandoned oil, gas or salt wells	Naturally occurring	>70% of original pressure likely to cause fractures; possibility of escape	Very high	High
Subterranean aquifers	Large capacity	Long-term consequences uncertain; possibility of escape	Low	High
Ocean – deep	Ultimate sink; very large capacity	Potential adverse effects on pH and marine life; very expensive; poor accessibility	Low	High (Liquid)
Ocean – mid-level	Ultimate sink; very large capacity	Potential adverse effects on pH and marine life; very expensive; poor accessibility; possibility of escape	Low	High (Liquid)
Green sequestration	Rebuilds forests; land management	Short duration – 1 year – 50 years; accounting is difficult	High	None
Solid carbonates	Stability for millions of years; surface storage; sufficient capacity	Very safe; naturally occurring	Low; Needs technology advancement	High; Possibly moderate

In one of these processes metal silicate rocks are converted, albeit incredibly slowly, to metal carbonates and silicon dioxides. This traps the CO₂ in its lowest energy and most stable form. The thermodynamics are favorable. Conversion of CO₂ to a metal CO₃ releases 60-180 kJ/mole compared to the 400 kJ/mole released in the transformation of C to CO₂ [Lackner et al, 1995]. Additionally, all the sequestration options the formation of

carbonates alone suffers no risk of release or of imposing unfamiliar changes on the ecosystem. In addition the material can be stored either in salt domes or on the surface in the same open-pit mines from which the mother material was obtained.

One of the early approaches explored towards achieving this chemistry was to react finely ground serpentine (MgSiO₃), a member of the ultramafic family of minerals, with carbonated water at 550°C for 3h [Dragelescu et al, 1972]. They observed that serpentine lost 60.5% of its MgO during this time. Zhang et al [1996] and Kojima et al [1997] correlated the grain size and the rate of reaction. As expected, they found that reaction rate was related to surface area. More recently, Ennick et al., [2001] reacted super critical CO₂ with a variety of metal salts found in aluminum production tailings. For example, they could react about 30% of the metal found in electric arc furnace dust to form carbonates.

In a different vein, O'Connor et al [2001] reported that an effective way to react serpentine was first to heat it (630°C for 1h at 1 atm) and then to react it (24h at 115 atm and 185°C). Serpentine consists of flat plates of Mg(OH)₂ and SiO₃ bonded via water molecules. By heating the finely ground material the water is displaced creating space for the newly delivered CO₂ provided as CO₂ or as bicarbonate. While the energy costs to accomplish this reaction are significant the 80% carbonation of the metal silicate was accomplished in 60 minutes at 185°C and 150 atm.

Thus, the issue remains. How does one react CO₂ with metal silicates at reasonable temperature and pressure, in a continuous manner, without creating significant amounts of CO₂ pollution, at a speed, in sufficient quantity and at low enough cost to be a candidate means for CO₂ sequestration?

By observing nature we have developed a new, simple and efficient means of generating metal carbonates from metal silicates. Exact costs will not be known until field studies are carried out. It does not impose significant environmental or safety impacts allowing rapid acceptance and utilization.

We will report on a new approach to promoting this reaction. In this design finely ground metal silicate rock, members of the ultramafic family of minerals, are treated in such a manner to greatly promote the reaction rate towards the point that it could be used commercially and cost competitively for the safe and rapid sequestration of CO₂.

SUMMARY

Of the options listed above (Strategies for GHG Reduction) we conclude that:

- 1) Option 1 is being engaged though the process is slow and a stabilization in world population is not expected to occur until sometime between 2050 and 2100.
- 2) Option 2 does not match human nature and is not acceptable geopolitically. Rather standards of living are increasing throughout the world and this trend is expected to continue.
- 3) Options 3, 4, and 5 are being examined and exercised though major changes in economic models, reduction in sociological anxieties and continued large investment

in technology. Each of these should contribute greatly to utilizing these options to best merit but all together these approaches are unlikely to halt CO₂ accumulation.

- 4) Thus, option 6 is required if global CO₂ levels are to be brought under control. Furthermore, while many options for capture and sequestration exist, the most promising are CO₂ capture using contained liquid membrane reactors and sequestration as metal carbonates. It is these technologies that we are developing.

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