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Compensation of Atmospheric CO_2 Buildup through Engineered Chemical Sinkage

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Abstract. Retrieval of background carbon dioxide into regional chemical extractors would counter anthropogenic inputs in a manner friendly to established industries. We demonstrate via atmospheric transport/scaling calculations that for idealized flat removal units, global coverage could be less than two hundred thousand square kilometers. The disrupted area drops to a small fraction of this with engineering into the vertical to bypass laminarity. Fence structures and artificial roughness elements can both be conceived. Sink thermodynamics are analyzed by taking calcium hydroxide as a sample reactant. Energy costs could be minimized at near the endothermicity of binding reversal. In the calcium case the value is 25 kcal mole^{-1}, as against a fuel carbon content of 150 in the same units. Aqueous kinetics are less than favorable for the hydroxide, but misting could counteract slow liquid phase transfer. Properties of superior scrubbers are outlined.

1. Introduction

Carbon management promises to evolve into a global scale industry during the coming era of climate change (e.g. Socolow et al., 1997). Carbon dioxide which would otherwise drive greenhouse warming will be intentionally stored in reservoirs as diverse as the terrestrial biosphere, the lithosphere, aquifers and the deep sea. Some plans for the manipulation of fossil fuel combustion products call for capture from stationary source effluent. However, the global vehicle fleet is a growing contributor to the CO_2 budget (Cutter Information, 1992). Auto exhaust is difficult to process and the world's gasoline distribution system will prove highly inertial. Downwind carbon removal concepts are benign relative to inertial industries and include farming of tree plantations and the surface ocean. Here we discuss a related but understudied option -reaction of carbonic acid into large and efficient chemical sinks (Lackner and Wendt, 1995). Our strategy is to overview the timing and dynamics of atmospheric transport involved, then to discuss thermochemistry and kinetic limitations. We conclude that transfer rates and overall energetics of the proposition need not be prohibitive. Comparisons are drawn with natural photosynthetic systems and with more familiar large scale engineering projects.

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2. Calculations

Ultimately the details of real, distributed removal facilities must be considered. However, it is useful to work forward in complexity from some simple conceptual analogs. We begin by asking if a perfect, flat sink could extract carbon dioxide at an adequate pace. The area disturbed in order to compensate fossil fuel burning will be computed. Over much of the planet the dominant winds are geostrophic and westerly (Riehl, 1972). At the surface, horizontal velocities are near 1 m s^{-1}. Averages in the planetary boundary layer and free troposphere are roughly 10 and 30 m s^{-1} respectively. We imagine a strip of completely absorbent material running north/south and from pole to pole. If it were 100 kilometers wide the residence time of the air above would be 10^4 seconds in the lower atmosphere. A column passing over the sink loses CO_2 from the bottom up, and steady state is achieved within local vertical mixing times. Removal may then be portrayed as a serial resistance process. Flux matching working away from the surface with elimination of variables indicates that the slow transfer step dominates. Some relevant constants are listed in Table 1. Molecular and eddy diffusivities for the computations are taken from Seinfeld (1986). In our crude analysis, the main barrier to transport through the lower atmosphere is micrometeorological, lying in the laminar layer just above the sink substance. For the moment we consider the free troposphere to be isolated. At a 1 cm s^{-1} transfer velocity, the hundred kilometer wide absorber may pull 10 percent of CO_2 from the boundary layer during a single transit. In darkness turbulence is suppressed and the first few hundred meters become an obstacle as well. Average removal from the lowest kilometer is 5 percent. Backfilling from the free troposphere occurs at the rate of internal mixing, or, within a few hours.

The boundary layer contains about a tenth of both the total atmospheric mass and its 350 ppm carbon dioxide content. One complete (diurnally averaged) pass over the hypothetical sink we have postulated may thus sequester four of the current loading of seven hundred Gt C (IPCC, 1995). The general

Table 1. Vertical transport characteristics near the surface.

	Laminar Layer	Boundary Layer	Free Troposphere
Thickness (cm)	0.01 - 0.1	10^5	10^6
Diffusivity (cm^2 s^{-1})	0.1 (molecular)	10^6 in daytime	10^5
Transfer (cm s^{-1})	1 - 10	10 in daytime slow at night	0.1
Internal Mixing (s)	0.001 - 0.1	10^4	10^7

circulation moves the entire midlatitude atmosphere in a circuit around the globe about twenty five times per year (Riehl, 1972). The 100 kilometer pole to pole absorber constitutes significant overkill; it captures almost 100 Gt C annually. This is ten times the anthropogenic input, so we are at liberty to reduce the north/south distance. The earth radius and circumference are 6000 and 40,000 kilometers. We imagine covering ten percent of the pole/pole distance (the geostrophic target) and distributing evenly between the hemispheres, which interchange relatively slowly. The thought experiment now consists of two rectangular sinks, each running a thousand kilometers along a meridian; one is located north of the equator and the other lies to the south. The extractors remove CO_2 from the lowest kilometer as westerlies pass across them. Horizontal diffusivities are small at the surface (10^4 m^2 s^{-1}; Seinfeld, 1986) but return takes place from the vertical and mixing across latitude bands is complete within months. The current human input of CO_2 is thus balanced.

Coverage required by the flat sink is extensive but less than synoptic. In each hemisphere the disturbed area corresponds roughly to the size of a large U.S. county. The conclusions drawn are independent of aspect ratio. Though spanning a shorter range of latitudes, a square patch 300 kilometers on a side removes more material from the boundary layer during a single column pass. A deeper shadow is created, but flow from its walls (diffusion inward) becomes more important in restoring CO_2 to the sink zone. Our heuristic analysis must of course be verified in global chemical tracer models, through numerical removal experiments. It appears, however, that given efficient absorption the footprint could be rendered manageable.

In fact the hundred thousand square kilometer value constitutes an upper limit. Geometries of the extraction devices will be subject to substantial manipulation, and laminarity restrictions can be circumvented by building upward. Roughness elements may be designed into or onto an absorbent to reduce thickness for the layer dominated by molecular diffusion. Variability in the natural atmosphere suggests a transfer velocity of 10 cm s^{-1} could be approached. The total area shrinks accordingly. It would also be possible to array sinks as a series of vertical surfaces (walls or fences). Experience dictates that structures as tall as ten meters could be constructed and maintained over large horizontal distances. This is one percent of our standard, round figure boundary layer height so that ten units removing carbon dioxide on contact match the rates derived above for 100 kilometers of flat material. Again backfilling is complete inside of local mixing times. The latter are difficult to define in the air nearest the planet because turbulence and eddy diffusivity are strong functions of altitude and instantaneous meteorological conditions (Seinfeld, 1986). Tracer plumes originating in the ten meter regime typically dilute downward in on the order of 10 to 1000 seconds (Sutton, 1977). A carbon dioxide shadow will behave similarly. Parcels in the lower boundary layer travel well under ten kilometers before the fence line can reasonably be repeated. The potential exists both for fractional coverage within the disruption zone and reduction of total length in the direction of the mean wind.

Artificial roughness elements and absorbent fences will alter the momentum budget of the lower atmosphere. Self consistent calculation of the velocity profile lies beyond the scope of the present work. It is clear, however, that yet another scale of atmospheric transport modeling is in order -the micrometeorological. Horizontal diffusion might be exploited to further reduce the footprint of extraction devices. A material absorption cross section will exceed the physical target size for multidimensional objects because CO_2 can transfer to their sides during passage. This effect may be minor but remains to be explored.

Table 2. Standard enthalpies and free energies of reaction for a carbon dioxide/calcium hydroxide cycle. Units are kcal $mole^{-1}$.

	Reaction			$\Delta H^\circ rx$	$\Delta G^\circ rx$
1	$CO_2(g) + Ca^{2+} + 2OH^-$	->	$CaCO_3(s) + H_2O(l)$	-22.9	-24.8
2	$CaCO_3(s)$	->	$CaO(s) + CO_2(g)$	42.7	31.2
3	$CaO(s) + H_2O(l)$	->	$Ca^{2+} + 2OH^-$	-19.8	-6.4
	Net Null			0	0

Carbon dioxide acts as an acid in aqueous solution and so is neutralized by strong alkali. A common reactant is calcium hydroxide. The saturated reagent serves as a standard pH 12 buffer, but must be kept isolated from the atmosphere to avoid calcium carbonate formation (Meites, 1963). In the laboratory, turbidity is often taken as a signal that fresh solution is needed. We will use $Ca(OH)_2$ as a proof of principle base here. 0.03 molar solutions can be prepared at room temperature. Thermodynamics are well understood for the carbonate and related species. Calcium must be recycled in a sustainable system and the CO_2 must be captured, at least effectively. A chemical sequence which achieves these goals is outlined in Table 2. Values for the major state functions are obtained from Perry and Chilton (1973). The enthalpy and free energy changes are standard; they refer to the passage of one mole of carbon through each of the reactions, and to reactants and products at 1 atmosphere pressure or unit molarity. Water is excluded because it is the solvent, and the solids are assigned unit activity. Fortuitously, concentrations in the system we have sketched fall near the standard values. The position of equilibrium may be computed for reaction 1. It is highly spontaneous under ambient conditions. Because CO_2 is likely hydrated near the liquid surface, the heat release (exothermicity) may be difficult to harvest. Le Chatelier's principle indicates that pure carbon dioxide can be recovered through reaction 2 if it is carried out at high temperature. Assuming a constant delta enthalpy and integrating over T, the equilibrium constant approaches unity at 1000 degrees Kelvin. The process there becomes spontaneous. We will not attempt to incorporate C_p adjustments. With proper insulation of the reaction vessel and a well designed heat exchange system, it should be possible to approach the endothermicity of 2 as the sole energy input. The carbon dioxide could be collected as a pure stream at atmospheric pressure, and the standard enthalpy is the relevant quantity. Rehydration to the hydroxide could be performed under controlled conditions and the heat output retained. The total energy cost for the Table 2 cycle might be kept to as little as 25 kcal $mole^{-1}$.

The petroleum based fuels generate about 150 kcal per mole of carbon on combustion. Even in the arbitrarily selected calcium case, the energetics are thus workable. Over a closed cycle the state functions cannot change their values and delta zeroes should be obtained, as reflected in the table. However, on a net basis we wish to concentrate CO_2 from 350 ppm to a full atmosphere of pressure. This reverse-mixing process hides a small entropic cost. It is best described as a free energy change and has the value $-nRT(X\ln X)$ where n is the total number of moles of air and X is the initial carbon mole fraction. For 350 ppm the value is 5 kcal $mole^{-1}$.

Diffusion controlled bimolecular reaction has the rate constant 10^{10} l $mole^{-1}$ s^{-1} in water (Stumm and Morgan, 1981). A typical Lewis base can easily be present at unit molarity. Aqueous molecular diffusivities are on the order of 10^{-5} cm^2 s^{-1}. In a one dimensional diffusion model of the sink column with loss rates maximized, the scale depth is a fraction of a micron and vertical transfer exhibits a piston velocity of several hundred cm s^{-1}. Clearly, processing in the liquid need not limit overall uptake. In alkaline solutions direct reaction with hydroxide anion is the fastest channel into the proton exchange network, and CO_3^{2-} is the stablest carbon species. If Ca^{2+} is the conjugate cation carbonate will locate it rapidly and generate calcite, the solubility product being 10^{-8}. Flocculent solid and precipitate formation are likely. The hydration ($CO_2 + OH^-$) rate constant is 10^4 l $mole^{-1}$ s^{-1}. A one dimensional scale depth of about a micron is derived, well under laminar layer thicknesses for natural bodies of fresh and salt water (Broecker and Peng, 1984). The Henry's Law constant of the carbon dioxide molecule is close to unity (Seinfeld, 1986). Piston velocities drop several orders of magnitude relative to diffusion control. For saturated reagent the value is of the order 0.1 cm s^{-1}.

Both gas and liquid phase restrictions can be avoided by misting the calcium hydroxide solution. Since an aerosol must be generated above the surface, this is in part a variation on the verticality theme. Air entering the sink zone would be sprayed with $Ca(OH)_2$ containing droplets. Roughly 10 meters of elevation are again achievable. The cost effectiveness of wind farming suggests that the capital outlay for towers would be practical. We take natural cloud properties as a reference point for mist design (Seinfeld, 1986). A low end but round figure radius for cloud particles is 10 microns. An individual drop volume is then about 10^{-9} cm^3 and a thousand particles per cubic centimeter gives the volume ratio 10^{-6} relative to air; 1 gram H_2O m^{-3} is an average cloud mass density. The global CO_2 concentration is 10^{-5} in units of molarity. If calcium hydroxide were present at 10^{-2} molar in one millionth of the volume of an air parcel, removal would be reagent limited. It is also the case that real cloud droplets sediment only slowly. In an artificial system it is possible to select the size distribution. 100 micron particles have individual volumes of $>10^{-6}$ cm^3. At 1000 cm^{-3} the volume ratio against the gas phase is $>10^{-3}$. Calcium is now available in excess. Each particle has 10^{-3} cm^2 of surface area and the total is 1 cm^2 of interface cm^{-3}. The diameter is sufficiently large that the one dimensional liquid phase model applies. The 0.1 cm s^{-1} diffusion/reaction velocity is in force within the droplets, and the lifetime of CO_2 in the vapor is 10 s. Under Stokes-Cunningham theory the 100 micron particles settle at 100 cm s^{-1}. Released in a curtain at the sink threshold, the droplets both absorb CO_2 and sediment in well under a minute. Downwind the logic developed for sequential walls/fences applies. Fetch and fractional disruption of the surface may be minimized by comparison with the flat sink analog.

Our particle dynamics computations amount to conceptual finite differencing. Basically, we submit that fast local removal can be attained by increasing contact with the absorbent interface. Spacing of the spray devices would be optimized to conserve water, and the work associated with lifting is minimal. The 10^{-5} moles of gas phase CO_2 present in a liter of air dissolve into 10^{-3} liters of the alkali. 100 kilograms of hydroxide solution chaperon each mole of carbon. Multiplying by the gravitational constant and the vertical distance, only a few kcal are consumed.

Having examined the calcium hydroxide baseline, we may now ask whether other scrubbing or binding agents would perhaps be superior. Agents will be sought which react rapidly but exert only a nominal hold on the carbon dioxide. The idealized removal/capture cycle is 1a) $CO_2 + L \to CO_2L$ followed by 2a) $CO_2L \to CO_2 + L$, where L signifies an as yet unknown ligand. Appropriate thermodynamic reasoning parallels that for 1 through 3; the L reactions are simply mirror images. Assuming weak complexation in the sense of chemical free energy, enthalpy and entropy trade off against one another. If endothermicity of the ligand/carbon release process 2a is low energy efficiency and cost are improved, but the engineer loses his/her ability to alter the position of equilibrium by raising temperature. If 2a entails a large heat input, the positive enthalpy change might still be balanced by disordering of the solute/solvent couple. Ligand and complex are then designed to achieve this effect.

3. Discussion and Conclusion

Photosynthesis constitutes an instructive analog to the removal systems we describe. Between 10^{-4} and 10^{-3} mole CO_2 m^{-2} s^{-1} could potentially flux into the earth's surface under 1 to 0.1 s cm^{-1} of serial resistance, the common atmospheric range (Seinfeld, 1986). Given the enthalpic content of typical plant tissue (120 kcal per mole of carbon; Drysdale, 1985), 50 to 500 W m^{-2} of light energy could be stored. The solar constant is 1400 W m^{-2}. With atmospheric attenuation, angle/surface geometry and a diurnal cycle all affecting the incoming spectrum, light limitation often plays into biological production rates. On the continents, water can be in short supply as well. The 10^{-4} mole CO_2 m^{-2} s^{-1} translates to 40 kg C m^{-2} y^{-1}, the rate postulated above for a flat extractor. Even the most prolific terrestrial ecosystems fix only one or two kg C m^{-2} annually. Tropical forests/wetlands and managed (agricultural) ecosystems tend to head lists of productivity (Schlesinger, 1997). Clearly the physiology of land plants would have to be altered significantly in order for them to compete on an areal basis with fast chemical sinkage. Quality soils and optimal precipitation patterns might not coincide with preferred sequestration sites. Engineered absorbers could intentionally be built near the safest storage compartments.

Marine ecosystems tend to be limited by trace nutrient upwelling (IPCC, 1995). Although large portions of the surface ocean are poor in either nitrogen or iron and could be fertilized, maximum production rates are very low. Only 10 Gt C y^{-1} are drawn down to the deep sea from all surface waters on the planet. Basin scale mixed layer volumes would have to be manipulated to exceed Gt levels of sequestration. The Southern Ocean and equatorial Pacific are currently under consideration for major fertilization experiments. Surface seawater is only slightly alkaline (pH 8). CO_2 hydrates through direct reaction with the water molecule in this regime, and the unimolecular time constant is 30 s. The removal scale depth extends to hundreds of microns given molecular diffusivity. Transfer across the liquid laminar layer dominates, with a piston velocity on the order of 0.005 cm s^{-1} (Broecker and Peng, 1984).

While the approach we outline for carbon dioxide retrieval appears feasible from a preliminary standpoint, considerable research would be required to move toward large scale testing or implementation. Global, micrometeorological and microkinetic modeling should be undertaken for the chemistry transport involved. Construction of bench top system mockups will be an early priority. Engineering hurdles implied in the collection of Gt levels of product material may prove difficult to surmount. Gathering and kilning of the resulting solids over regional geographic scales would constitute a significant challenge to the carbon management industry. Conveying CO_2 to the ultimate sink locations will be a design and energy intensive problem, but it is one which is common to other capture/sequestration technologies.

Environmental and policy considerations to be associated with the chemical extractors will be quite complex. Potential secondary effects must be extensively surveyed. Under some configurations for the removal facilities, carbon dioxide shading would be significant and could affect plant growth downrange. A small negative feedback ensues if the targeted areas are biologically productive. Both natural and managed ecosystems would be subject to large scale perturbation. Impacts could be deemed objectionable in either case but in an integrated assessment would have to be weighed against the risks of greenhouse warming. Furthermore, substantial flexibility exists in siting decisions. Many substances would be depleted from the atmosphere incidentally. Examples include the nitrogen, sulfur and organic acids. Regional photochemistry would be altered. Changes in local hydrology would probably resemble those introduced by a large reservoir. The estimated physical scope of disturbance is comparable to many well documented intra- and international engineering projects. The U.S. highway network and Three Gorges dam/reservoir constitute prominent examples from the last few decades (WRI, 1992). Many human cultures have managed agricultural landscapes tens of thousands of square kilometers in extent (Brown, 1995). As the era of global change unfolds, regional removal facilities may well prove acceptable. They will be particularly attractive if they are nonthreatening to inertial energy use infrastructures.

The concept explored here for engineered chemical absorption of carbon dioxide stands alone and can be implemented remote from all modes of emission. We have shown that it does not entail obvious transport or thermodynamic limitations. Under the well known constraints imposed by the second law of thermodynamics, this may be viewed as something of a surprise. CO_2 dispersed through the entirety of the troposphere may not be impossible to retrieve through human intervention. In fact under the arguments we have developed the global wind provides for motion, and bonding energy is harnessed to surmount entropic barriers. If the overall thermodynamic costs approach ten percent of the fossil fuel carbon content, a chemical removal system might be economically viable. We conclude that further study is warranted.

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