

## ***Link Foundation Fellowship Final Report for Kurt Zenz House***

### ***Introduction***

The increasing concentration of carbon dioxide (CO<sub>2</sub>) in the atmosphere due to the combustion of fossil carbon is changing the Earth's climate system [1]. The threat of climate change coupled with the accelerating demand for primary energy has stimulated research into technologies that limit CO<sub>2</sub> emissions from fossil carbon power plants and into technologies that remove CO<sub>2</sub> from the atmosphere [2]. One of the most promising technologies under investigation to limit CO<sub>2</sub> emissions from power plants is CO<sub>2</sub> sequestration. CO<sub>2</sub> sequestration involves separating CO<sub>2</sub> from N<sub>2</sub> after combustion and injecting the CO<sub>2</sub> into a geologic formation for long-term storage.

An essential problem of CO<sub>2</sub> capture and storage technologies is finding sufficiently large geologic depositories to store the captured anthropogenic CO<sub>2</sub>. Additionally, due to the subsurface temperature profile of terrestrial storage sites, CO<sub>2</sub> stored in these reservoirs is buoyant. As a result, a portion of the injected CO<sub>2</sub> can escape if the reservoir is not appropriately sealed. In addition, CO<sub>2</sub> capture with geologic storage can only serve to limit the rate of rise of CO<sub>2</sub> concentrations. To decrease the concentration of atmospheric CO<sub>2</sub>, processes must be developed to remove CO<sub>2</sub> directly from the atmosphere. The central objective of my Link Foundation supported research was to explore new approaches to storing captured CO<sub>2</sub> and for removing CO<sub>2</sub> from the atmosphere.

### ***Results-Storage of captured CO<sub>2</sub> in deep-sea sediments***

The majority of my Link Foundation supported work has focused on storing captured anthropogenic CO<sub>2</sub> in deep-sea sediments. My work has demonstrated that injecting CO<sub>2</sub> into deep-sea sediments below 3000 m water depth and a few hundred meters of sediment provides permanent geologic storage even with large geomechanical perturbations [3]. At the high pressures and low temperatures common in deep-sea sediments, CO<sub>2</sub> resides in its liquid phase and can be denser than the overlying pore-fluid causing the injected CO<sub>2</sub> to be gravitationally stable.

The geothermal gradient, which varies from ~0.02°C/m to ~0.04°C/m, controls changes in the density of CO<sub>2</sub> injected into deep-sea sediments by expanding and contracting the mobile CO<sub>2</sub> until its density equals the density of the surrounding pore-fluid. Given a seafloor depth of 3500 meters and a geothermal gradient of .03°C/m, the injected CO<sub>2</sub> becomes neutrally buoyant at ~200 m below the seafloor [4]. Above the sediment depth of neutral buoyancy, the CO<sub>2</sub> is denser than the ambient pore-fluid. We have labeled this range between the seafloor and the sediment depth of neutral buoyancy as the negative buoyancy zone (NBZ). That acronym has since become a part of the field's lexicon [see [5]].

Additionally, CO<sub>2</sub>-hydrate formation will impede the flow of CO<sub>2</sub>, and serve as a second cap on the system. The high pressures and low temperatures necessary to compress CO<sub>2</sub> to greater density than the pore-fluid are similar to the conditions necessary for CO<sub>2</sub>-hydrates to form. CO<sub>2</sub>-hydrates (5.75H<sub>2</sub>O·CO<sub>2</sub>) are non-stoichiometric crystalline compounds that form by trapping CO<sub>2</sub> molecules in hydrogen-bonded cages of H<sub>2</sub>O [6]. These compounds occur in a 3-phase meta-stable equilibrium between CO<sub>2</sub>(l), CO<sub>2</sub>(aq), and CO<sub>2</sub>-hydrate [7]. We refer to the sub-seafloor region with low enough temperatures and high enough pressures for hydrate formation as the *hydrate formation zone* (HFZ).

The HFZ extends from the seafloor downward into the sediment until the temperature rises above the boundary of the hydrate stability field. The relative location of the NBZ and the HFZ layers and the injected CO<sub>2</sub> ensures inherently stable CO<sub>2</sub> storage. My work has demonstrated that to ensure maximum storage stability, CO<sub>2</sub> should be injected below the sediment layer where CO<sub>2</sub>-hydrates form and below the sediment layer of less dense pore-fluid.

I have developed several models to analyze the flow of CO<sub>2</sub> on the injection time-scale, the formation and dissolution of CO<sub>2</sub>-hydrates, and the dilution of the CO<sub>2</sub>(aq) solution by diffusion. The modeling work has constrained the time-scales for each of these physical processes, and it has shown that although the injection will perturb the geothermal gradient above the injection zone, hydrate trapping and gravitational trapping will nevertheless occur on the injection timescale [to be detailed in my next publication].

My work has further demonstrated that a 300 meters thick CO<sub>2</sub> storage site of 50% porosity and 50% residual water could store total annual U.S. CO<sub>2</sub> emissions (~8 Gt of CO<sub>2</sub>) in a ~80 km<sup>2</sup> area. Indeed, over ~22% (1.3 M km<sup>2</sup>) of the seafloor within the economic zone of the continental U.S. is appropriate for gravitational trapping of CO<sub>2</sub> storage [8]. That represents over 10<sup>4</sup> Gt of inherently stable CO<sub>2</sub> storage.

Two potential limitations for storing captured CO<sub>2</sub> in deep-sea sediments are the permeability of those sediments and the risk of over-pressuring the sediments and creating mud volcanoes. A study of the literature indicates plentiful sediments with intrinsic permeabilities in the 10<sup>-15</sup> m<sup>2</sup> range exist [9]. To inject all the CO<sub>2</sub> generated by 1 GW of coal fired power plant into deep-sea sediments of that permeability while keeping the pore pressure below that of the least compressive stress requires ~ 5 km of horizontal ocean pipeline injection zone. The U.S. has about 200 GW of coal fired power installed near coastlines. Thus, 1000 km of horizontal injection zone could inject all the CO<sub>2</sub> generated by U.S. coal-fired coastal power plants into low-permeability deep-sea sediments for storage. For sediments of higher permeability, less horizontal piping would be required.

### ***Results—Electrochemical acceleration of chemical weathering***

In addition to my work on storing CO<sub>2</sub> in deep-sea sediments, I developed an electrochemical process that accelerates natural chemical weathering. This process enables atmospheric CO<sub>2</sub> to be captured directly and stored primarily as HCO<sub>3</sub><sup>-</sup> in the ocean without further acidifying the ocean.

The process involves removing HCl from the ocean and neutralizing the acid through reactions with silicate rocks. The increase in ocean alkalinity resulting from the removal of HCl causes atmospheric CO<sub>2</sub> to dissolve into the ocean. Most of the additional alkalinity will likely lead to precipitation or enhanced preservation of CaCO<sub>3</sub> resulting in the permanent storage of the associated carbon and the return of an equal amount of carbon to the atmosphere. The products of the neutralization reaction between silicate rock the removed HCl can flow back to the ocean. After the neutralization, the net reaction is identical to the natural silicate weathering reaction. The natural silicate weathering process, however, is driven primarily by carbonic acid while the engineered process accelerates the weathering kinetics to industrial rates by replacing this weak acid with strong HCl. Harvard University has filed a patent on this process.

My work demonstrates that in the thermodynamic limit—and with the appropriate silicate rocks—the overall reaction is spontaneous. It is not surprising that the net reaction is spontaneous because it is the natural silicate weathering reaction. A range of efficiency scenarios indicates that in practice the process will require between 150 - 600 kJ of work per mol of CO<sub>2</sub> captured and stored. The process can be powered from stranded energy sources too remote to be useful for the direct needs of population centers.

The magnitude of the CO<sub>2</sub> problem is daunting, and offsetting even ~15% of global emissions by electrolysis of seawater would be a serious task. To offset ~15% of annual carbon emissions (~3.7 gigatonnes CO<sub>2</sub> or 1 gigatonne of carbon) ~10<sup>14</sup> moles of HCl would have to be removed from the ocean and neutralized per year. Seawater would have to be separated into acid and base at a global volumetric flow rate of ~6000 m<sup>3</sup>/s. Large sewage treatment facilities have a capacity of ~60 m<sup>3</sup>/s [10]. Thus, capturing and storing 3.7 gigatonnes of CO<sub>2</sub> annually by the process we discuss would require ~100 plants with a volumetric flow capacity similar to that of large sewage treatment facilities.

Careful analysis of the likely costs of *electrochemical weathering* indicates that the process will be expensive. It is unlikely to compete with emission reductions. Additionally, removing CO<sub>2</sub> from the air through biomass combustion with CO<sub>2</sub> capture and storage (CCS) is likely to be a cheaper option for removing CO<sub>2</sub> from the air. Land and water use issues, however, may limit deployment of biomass combustion with CCS. *Electrochemical weathering* could be useful, however, if emissions reductions do not materialize and the deployment of biomass combustion with CCS is limited.

### ***Significance and Impact***

My Link Foundation supported work has focused on a new approach for storing captured CO<sub>2</sub> and a new approach to remove CO<sub>2</sub> from the atmosphere. The former work has demonstrated that storing liquid CO<sub>2</sub> in deep-sea sediments can be inherently secure while the latter work has demonstrated the energetic feasibility of electrochemically accelerating chemical weathering to remove CO<sub>2</sub> directly from the atmosphere. My work achieved its objectives of identifying an inherently stable approach for CO<sub>2</sub> storage and a new approach to remove CO<sub>2</sub> from the air.

Deep-sea sediments appear to be an attractive option for CO<sub>2</sub> storage since they provide both an inherently stable option for CO<sub>2</sub> storage and an enormous resource base. The electrochemical weathering work has demonstrated that accelerated natural chemical weathering is technically feasible. It appears unlikely, however, to be a cost-effective approach for climate change mitigation unless the rapid climate change requires the immediate need to reduce atmospheric concentrations of CO<sub>2</sub>.

### ***Where might this lead***

I continue to research both elements of my Link Foundation supported research. In the near future, I will be focusing primarily on the geomechanics associated with injecting large quantities of CO<sub>2</sub> into deep-sea sediments. A group of independent power producers has approached my advisor and me about building an integrated gasification combined cycle power plant on the east coast of the United States that injected part of its produced CO<sub>2</sub> into deep-sea sediments. That collaboration is particularly exciting as it may lead to the first large scale project based on my Link Foundation supported research.

### **Publication list**

1. House, K. Z.; Schrag, D.; Harvey, C.; Lackner, K., Permanent carbon dioxide storage in deep sea sediments. *Proceedings of the National Academy of Sciences* 2006, 103, (33), 1291-1295.
2. House, K. Z.; House, C. H.; Schrag, D. P.; Aziz, M. J., Electrochemical Acceleration of Chemical Weathering as an Energetically Feasible Approach to Mitigating Anthropogenic Climate Change. *Environmental Science & Technology* 2007.
3. House, K.Z.; Harvey, C.; Schrag, D.; The Geomechanics and Long Term Evolution of CO<sub>2</sub> Injected into Deep-sea Sediments [In prep]

### **Use of Discretionary funds**

The discretionary funds were used for three primary purposes. First, a license for the numerical package COMSOL (\$2500.00) was purchased. Next, a computer dedicated primarily to modeling fluid flow of CO<sub>2</sub> injected into deep-sea sediments was purchased. Finally, several reference books including, *Theory of Fluid Flows Through Natural Rocks*, *Upscaling Multiphase Flow in Porous Media*, *Natural Gas Hydrates* etc. were purchased.

### **How the Link Fellowship Made a Difference**

First and foremost, the Link Fellowship enabled me to pursue a line of research not tied specifically to an advisor's grant. My work certainly complimented one of my advisor's grants, but my work was sufficiently different that it might not have been possible without the Link support. That flexibility enabled me to experiment with less well established ideas. As a result, I was able to publish two high profile papers on innovative approaches to mitigating climate change. Those papers achieved a fair amount of media attention. Articles about those papers have appeared in the *New York Times*, the *San Francisco Chronicle*, the *Boston Globe*, the *BBC*, etc. I do not believe that I would have been able to do as original work had I not had my Link Fellowship.

## References

1. IPCC, 2007: *Summary for Policymakers in: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. 2007, Cambridge, UK: Cambridge University Press.
2. Rubin, E., L. Meyer, and H. de Coninck, *IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change*. 2005, Intergovernmental Panel on Climate Change: Cambridge United Kingdom.
3. House, K.Z., et al., *Permanent carbon dioxide storage in deep sea sediments*. Proceedings of the National Academy of Sciences, 2006. **103**(33): p. 1291-1295.
4. Lemmon, E.W., M.O. McLinden, and D.G. Friend, *Thermophysical Properties of Fluid Systems*, in *NIST Chemistry WebBook*, P.J. Linstrom and W.G. Mallard, Editors. 2005, National Institute of Standards and Technology: Gaithersburg, MD.
5. Dornan, P., S. Alavi, and T.K. Woo, *Free energies of carbon dioxide sequestration and methane recovery in clathrate hydrates*. J. Chem. Phys. , 2007. **127**.
6. Lee, K.M., et al., *CO<sub>2</sub> hydrate behavior in the deep ocean sediment; phase equilibrium, formation kinetics, and solubility*. Geophysical Research Letters, 2002. **29**(21).
7. Diamond, L. and N. Akinfiev, *Solubility of CO<sub>2</sub> in Water from -1.5 to 100 C and from 0.1 to 100 Mpa: Evaluation of literature data and thermodynamic modelling*. Fluid Phase Equilibria, 2003. **208**: p. 265-290.
8. NASA. *Shuttle Radar Tomography Mission*. 2002 2003 [cited; Available from: <ftp://e0mss21u.ecs.nasa.gov/srtm/>].
9. Spinelli, G.A., E.R. Giambalvo, and A.T. Fisher, *Sediment permeability, distribution, and influence on fluxes in oceanic basement*, in *Hydrogeology of the Oceanic Lithosphere*. 2004, Cambridge University Press: Cambridge, U.K. p. pp. 151.
10. <http://www.mwrd.org/plants/default.htm#Stickney%20WRP>.