A Carbon Management Research Strategy

Donald J. DePaolo
Associate Laboratory Director for Energy Sciences, Lawrence Berkeley National Laboratory

Class of 1951 Professor of Geochemistry
University of California, Berkeley

Center for Nanoscale Control of Geologic CO₂
Outline

• Present carbon emissions and outlook. Humans in a pre-Human environment.
• The geologic view; what do we need to accomplish and when?
• Carbon intensity of energy production – ramping it down decade by decade
• CCS, Biofuels, and Artificial Photosynthesis.
• What about carbon Usage?
• Emphasis on aspects of the DOE R&D portfolio (it’s not so bad!)
Total Global Emissions are not slowing down

Source: CDIAC; Houghton et al 2012; Giglio et al 2013; Le Quéré et al 2014; Global Carbon Budget 2014
Near term outlook is not good

Economic growth based on IMF projections, fossil fuel intensity based on 10-year trend

Source: CDIAC; Friedlingstein et al 2014
And coal is King again….

Data: CDIAC/GCP

Growth rates 2012–2013

Coal 3.0%
Oil 1.4%
Gas 1.4%
Cement 4.7%

Source: CDIAC; Le Quéré et al 2014; Global Carbon Budget 2014
The most pessimistic IPCC 2005 projections of integrated carbon emissions now appear optimistic.
The next 100 years will make a huge difference

East Antarctic ice sheets unstable above 700 ppm CO$_2$
Turning the clock back….to pre-Human times

Atmospheric CO₂ based on δ¹⁸O

Antarctic Glaciation starts

Quaternary range (0 - 2 Ma)
Box model version of global carbon cycle

- Atmosphere: 600 Gt
- Terrestrial Biosphere: 600 Gt
- Terrestrial Soils: 1500 Gt
- Surface ocean: 1000 Gt
- Total Surface Reservoirs: 3700 Gt
- Deep Earth Reservoirs
- Ocean carbonate sediment

*Fluxes in Gt C/yr

Volcanoes (0.2 Gt C/yr)
Anthropogenic C emissions from fossil fuels first exceeded the geologic rates in the late 19th century. Now they are ca. 50x higher.

Data from ORNL database.

We are far beyond talking about natural or normal processes.
Carbon Intensity of Energy Production as Figure of Merit

-5 MtC/PWh/decade

800 PWh at 5 MtC/PWh = 4 GtC/yr
Carbon Energy Intensity as Figure of Merit

Extra 1000 Gt C emitted
Getting there – CCS would allow for large scale continued energy production from Coal and NG.

800 PWh at 5 MtC/PWh = 4 GtC/yr
Biofuels, AP, and even CO$_2$-EOR can help with liquid transportation fuels.
Coal and Natural gas use means CCS is a requirement.

- Vertical well
- Horizontal well
- Ground surface
- Potable aquifer
- CO₂ gas
- sc CO₂
- Free CO₂ phase
- Shale (caprock)
- Sandstone

1.5 - 3 km

20° C, 10 bar

60 - 100° C, 150 - 300 bar

10⁻⁴ to 10⁻⁷ Da
0.1 to 1 Da
DOE Energy Frontier Research Centers

The U.S. DOE Office of Fossil Energy has recognized the critical role that Carbon Capture and Sequestration must play in reducing the CO$_2$ released to the atmosphere over the next 100 years.

There are demonstration projects underway in many parts of the U.S. and internationally, but the DOE Office of Science has also put new resources into basic research in the form of EFRC’s.

1. **Nanoscale Controls on Geologic CO$_2$ (NCGC; LBNL lead)**
2. **Subsurface Energy Security (CFSES; Texas Austin lead)**
3. **Geological Storage of CO2 (GSCO2; U. Illinois lead)**
Some GCS basic research questions …..

Questions:

1. How much CO$_2$ is likely to be accounted for by capillary trapping? What does it depend on?

2. Is capillary trapping permanent, or can it break down on longer timescales due to chemical processes?

3. Will geochemical reactions affect the capacity and security of shale seals if they are fractured or faulted and/or fractured during injection?

4. Can a significant fraction of the injected CO$_2$ be converted to carbonate on a 1000-year time scale?
Attempting to deal with scales....
LBNL Major Research Facilities

- Advanced Light Source
- National Energy Research Scientific Computing Center
- Joint Bio-Energy Institute
- Molecular Foundry
- Solar Energy Research Center
- National Center for Electron Microscopy
Tools for advancing CCS technology

Leveraging DOE’s Science-Based Prediction Capability to Build Confidence in Engineered–Natural Systems

Carbon Capture Simulation Initiative (CCSI)
To accelerate the path from concept (bench) to deployment (commercial power plant) by lowering the technical risk in scale up.

National Risk Assessment Partnership (NRAP)
To accelerate the path to CCUS deployment through the use of science-based prediction to quantify storage-security relationships, thereby building confidence in key decisions.
NRAP: Science-based prediction to build confidence in storage security by quantifying system performance for multiple conditions.

NRAP Goal—to predict storage-site behavior from reservoir to receptor and from injection through long-term storage...

...in order to quantify key storage-security relationships for various site characteristics.

Confidence in uncertain predictions can be built through comprehensive, multi-organizational team assessments.

NRAP is building and applying computationally efficient tools to probe site behavior stochastically, thereby accounting for uncertainties and variability in storage-site characteristics.
Assessing risks in complex geosystems

**NRAP Goal**—to predict storage-site behavior from reservoir to receptor and from injection through long-term storage...

...in order to quantify key storage-security relationships for various site characteristics.

**Challenge**

- Large, complex system
- Uncertain geologic parameters
- Prediction of processes that cannot be directly tested or observed
- Site-specific characteristics

**NRAP Approach**

- Utilize integrated assessment models that break the system into smaller pieces
- Utilize reduced order models that run rapidly coupled with Monte Carlo methods
- Utilize high-fidelity, physics-based models to characterize critical behavior
- Build in flexibility for utilizing site-specific information, including data generated by reservoir simulators based on site models
Induced seismicity working group

1. Identify site characteristics and operations that lead to low-risk—i.e. minimal hazard, minimal damage.

2. Develop techniques to quickly identify and manage seismicity problems if they should appear.
CO$_2$ utilization – pipe dream or reality?

Current Research on Atmospheric and Captured CO$_2$ Utilization
Large scale “capture” and use of CO$_2$

Selectively use CO$_2$ from the atmosphere directly by natural or artificial photosynthesis; convert to fuels

Capture gases at source, purify CO$_2$
Low-Energy CO₂ Capture through Cooperative Adsorption

Scientific Achievement
An unprecedented cooperative mechanism for CO₂ capture via insertion into metal–amine bonds is revealed

Significance and Impact
Understanding the mechanism enables us to design new MOF adsorbents that can significantly reduce the energy required for CO₂ capture from a power plant flue gas

Research Details
– Insertion of CO₂ at one site facilitates insertion at a neighboring site, leading to formation of ammonium carbamate chains via a chain reaction
– The pressure of the step can be systematically tuned to minimize the energy of CO₂ separations

Top: As revealed by powder x-ray diffraction, CO₂ is adsorbed by mmen-Mn₂(dobpdc) via insertion into metal–amine bonds. One-dimensional chains of ammonium carbamate are formed as the cooperative process propagates along the pore surfaces.
Bottom: CO₂ adsorption isotherms at 25, 40, 50, and 75 °C for mmen-M₂(dobpdc) (M = Mg, Co) show how the position of the step can be controlled by varying metal-amine bond strength.

McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odoh, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Kyuho, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long
Nature 2015, http://dx.doi.org/10.1038/nature14327
Dangling amines coat the periphery of the channel leaving space for rapid CO\textsubscript{2} diffusion

McDonald, Lee, Mason, Wiers, Hong, Long J. Am. Chem. Soc. 2012, 134, 7056
For phase-change adsorbents, a small change in temperature gives a large working capacity.

McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odo, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Kyuho, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long Nature 2015, available online
One of three U.S. Department of Energy-supported National Bio-Energy Research Centers dedicated to enabling clean, carbon-neutral biofuels from cellulosic (non-food) biomass
JOINT BIOENERGY INSTITUTE

JBEI technology development & improvement strategy

- Increase C6/C5 ratio
- Lower lignin content
- Less enzyme use
- Lower IL price
- Lower IL use
- Increase biofuel yield
- Increase fermentation productivity
- +Lignin valorization

Objective – reduce biofuel cost from current $40 to ca. $3/gal
JBEI’s Research Approach is High Risk

JBEI approach

Genetically modified crops for optimized for biofuel production

Ionic liquid pretreatment process
• high yield saccharification of biomass
• low levels of inhibitors
• lignin valorization

Microbes engineered to produce drop-in fuels for all transportation segments

Less risky approach

Understanding current crops for use as biofuel feedstocks

Improvements to existing methods for biomass deconstruction

Incremental improvements in production costs of existing fuels (ethanol, butanol)
JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS (JCAP)

Aims to develop an efficient, scalable and robust prototype that generates fuel from sunlight, water, and carbon dioxide.

TYPES OF ARTIFICIAL PHOTOSYNTHESIS DEVICES

**PHOTOVOLTAIC + ELECTROLYZER**
- **Advantages:** Efficient and already developed
- **Challenges:** Expensive

**PARTICLE DISPERSIONS**
- **Advantages:** Low cost
- **Challenges:** Dangerous

**INTEGRATED SYSTEM**
- **Advantages:** Efficient and safe; potentially low cost
- **Challenges:** Earth-abundant materials undiscovered
Efficient TiO$_2$-protected amorphous Si photo-cathodes demonstrated

Stabilization of efficient earth-abundant photo-anodes at extreme pH by nanotexturing and catalyst overcoat

Discovery and demonstration of new class of NiFeCoCe oxygen evolution catalyst

Solar fuels generator demonstrated at neutral pH by electrolyte recirculation

Energy efficiency tradeoff between panel lifetime and device efficiency determined
JCAP transitions to the challenge of progress toward a solar fuels generator producing fuel from carbon dioxide, sunlight and water.
**JCAP RESEARCH THRUSTS**

1. **THRUST 1: Electrocatalysis**
   - **KEY SCIENTIFIC GAP**
     Understanding the structural and compositional parameters that govern the:
     - Activity and selectivity of CO₂RR catalysis, and
     - Activity and selectivity of OER catalysis
   - **KEY FOCUS**
     - Discovery and understanding of heterogeneous CO₂RR electrocatalysis
     - Discovery and understanding of heterogeneous OER electrocatalysis

2. **THRUST 2: Photocatalysis and light capture**
   - **KEY SCIENTIFIC GAP**
     Understanding the effect of (1) surface composition, (2) surface structure, and (3) electronic structure on the photocatalytic activity for CO₂RR and OER
   - **KEY FOCUS**
     - Discovery and understanding of CO₂RR and OER photocatalysis.
     - Development and understanding of light harvesting photonic architectures

3. **THRUST 3: Materials integration into components**
   - **KEY SCIENTIFIC GAP**
     Understanding of how interfacial phenomenon influence:
     - Light absorption and generation efficiency
     - (Photo)electrocatalytic activity
   - **KEY FOCUS**
     - Development and understanding of integrated catalyst/light absorber assemblies

4. **THRUST 4: Modeling, test-bed prototyping, & benchmarking**
   - **KEY SCIENTIFIC GAP**
     Understanding of how charge-and-ion-transport through components affects the efficiency of integrated devices
   - **KEY FOCUS**
     - Modeling and simulation of device parameters and test-bed architectures
     - Development and understanding of light harvesting photonic architectures
Engineered Geothermal Systems with scCO₂ as the working fluid phase

- **Heat extraction** rates with CO₂ are ≈50 % larger than for water.
- CO₂ is favorable in terms of wellbore hydraulics.
- Rock-fluid chemical interactions are weaker for dry, anhydrous CO₂ than for water.
- Fluid losses are costly for water, but could earn greenhouse gas storage credits for CO₂.

Field Demonstration Project, Cranfield Mississippi
B. Freifeld, LBNL
Summary

• Geologic carbon storage is necessary to get through the next 150 years with acceptable total carbon emissions

• Using CO$_2$ in large enough quantities to make a difference in emissions is challenging, but…

• Making fuels from sunlight and CO$_2$ is one way to do it – either with natural photosynthesis (cellulosic biofuels) or through artificial photosynthesis.

• EOR with supercritical captured anthropogenic CO$_2$ can contribute some reduction in carbon intensity in the next few decades

• Other possibilities, like Engineered Geothermal Systems (EGS) with scCO$_2$ are at early stages of evaluation
Taylor Glacier, Antarctica

Thank you