



# IN-SITU STUDY OF CARBON DIOXIDE SEQUESTRATION IN SALINE BRINE FORMATIONS

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## CO<sub>2</sub> Emissions from Fossil Fuels in 2001

(Giga Tons Carbon Equivalent)



**Worldwide**

6.568



**US**

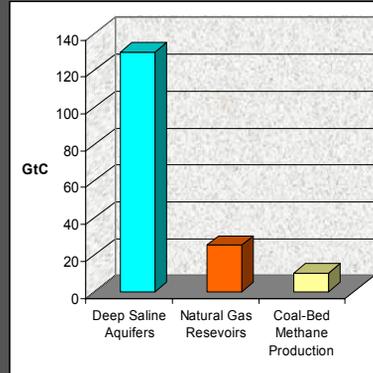
1.565

24% of the World's total CO<sub>2</sub> fossil fuel emissions

Source: eia.doe.gov

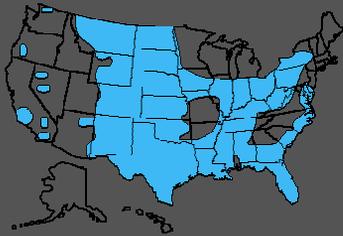
# Geologic Sequestration Options

- Saline Aquifers - hydrodynamic trapping
  - Also solubility trapping & mineral trapping
- Hydrocarbon Reservoirs - geologic trapping
  - Effective confining layer already determined
- Coal Beds – absorption



Source: [Carbon Sequestration Research and Development](#)

## Deep Saline Aquifers in the US



Source: US Geological Survey

- Depths greater than ~600 m
- Close to nearly all major CO<sub>2</sub> generators
- Greatest capacity of the geologic sequestration options (~130 GtC)
- Most technically challenging

# Site Selection & Criteria

Soft Criteria – Change on a human timescale

- Economic
- Political
- Societal
- Identify point sources of CO<sub>2</sub>
  - Output
  - Purity
  - Proximity

Hard Criteria – Change on a geologic timescale

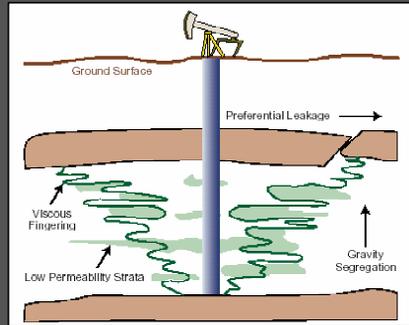
- Geology: Identify confining formations
- Hydrodynamics: Identify flow systems suitable for hydrodynamic trapping
- Geothermal and hydrostatic gradients

# Injection Well Requirements

- Underground Injection Control (UIC) Program – Safe Water Drinking Act of 1974
- Class I Injection – municipal or industrial waste (including hazardous) below the deepest USDW
- Monitoring requirements:
  - Monitoring wells only required after an identified potential leak
  - Continuous monitoring of injection pressure and flow rate
  - Additional tests at one and five year intervals

## CO<sub>2</sub> Properties affect Migration

- Density difference from that of brine leads to a buoyancy force.
- Low viscosity leads to viscous fingering.
- Dissolved CO<sub>2</sub> may dissolve minerals leading to an increase in permeability and porosity.



Source: [Carbon Sequestration Research and Development](#)

## Storage Mechanisms

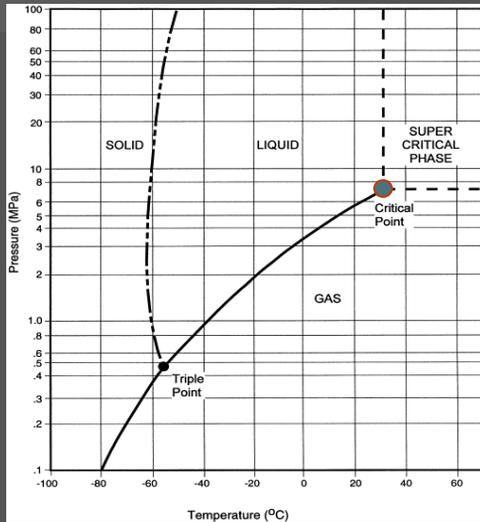
- Dissolved state in pore water
  - 1M salinity: 41-48 kg CO<sub>2</sub>/m<sup>3</sup>
  - 4M salinity: 24-29 kg CO<sub>2</sub>/m<sup>3</sup>
- Residual gas trapped by capillary forces
- Dense supercritical state
- Permanent state in a carbonate mineral

Source: Ennis-King, 2000

# CO<sub>2</sub> Phase Diagram

## Critical Point:

T = 31.1 °C  
 P = 7.38 MPa  
 (1070 psi)



Source: Bachu, 2000

## The Major Challenge...

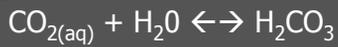
is discovering ways to optimize hydrodynamic trapping, while increasing the rate of carbonate formation.

Favoring Conditions			
	Temperature	Pressure	pH
<b>Dense Supercritical State</b> To maximize mass transfer and storage	Low	High	N/A
<b>Carbonate Precipitation</b> To immobilize and permanently store CO <sub>2</sub>	High	High	High

# Chemical Reactions



*CO<sub>2</sub> dissolves in water*



*Carbonic acid is formed (low pH, <5)*



*Bicarbonate is formed (mid pH, ~7)*



*Carbonate is formed (high pH, >9)*



→ *Calcite*



→ *Magnesite*



→ *Dolomite*



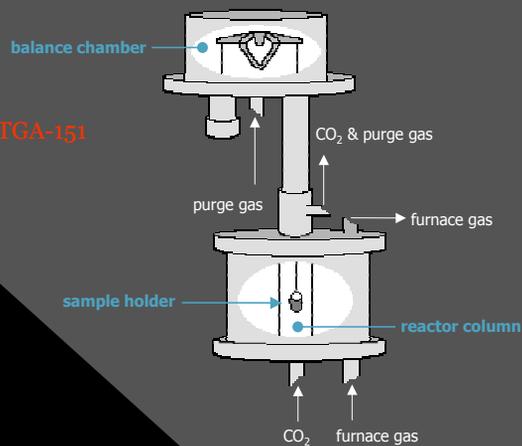
→ *Siderite*

Source: Soong, 2002

# High Pressure Thermo-Gravimetric Analyzer

CAHN TGA-151

The Energy Institute



## HP-TGA Specifications

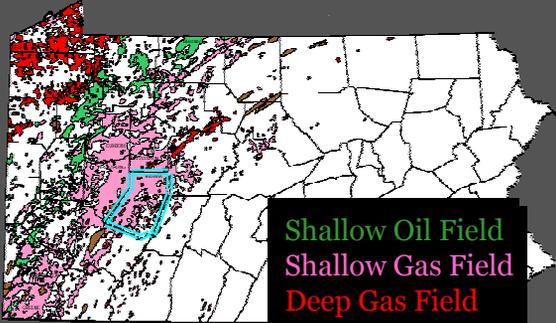
- Maximum pressure:
  - 1500 psi @ 25°C
  - 1000 psi @ 1000°C
- Temperature range:
  - 1100°C at ambient pressure
  - 1000°C at 1000 psi
- 1/8" Chromel-Alumel thermocouple
- Internal volume = 0.3 liters
- Maximum weight: 10g
  - Sensitivity: 1µg
  - Sensitivity decreases with high pressures

## Research Objectives

- Explore the solution kinetics of reactions of CO<sub>2</sub> and field brine
  - Pressure range: 200 – 1200 psi
  - Temperature range: 25 – 200 °C
  - pH range: 3 – 11
- To verify the efficiency and accuracy of thermo-gravimetric analysis
- Scale-up experimentation to a 500 ml CSTR to corroborate optimum conditions

# Experimental Field Brine

- Indiana County Gas Well
- Depth: 2,800 m
- Oriskany sandstone



Source: dcnr.state.pa.us

Shallow Oil Field  
 Shallow Gas Field  
 Deep Gas Field  
 Gas Storage Areas

Metal	mg/l
Al	6.84
Ba	789
<b>Ca</b>	<b>23,600</b>
<b>Fe</b>	<b>223</b>
K	1,170
<b>Mg</b>	<b>1,440</b>
Mn	5.26
Na	44,900
P	< 2
S	13.1
Si	< 10
Sr	8,910

Metals of greatest concern for carbonate formation

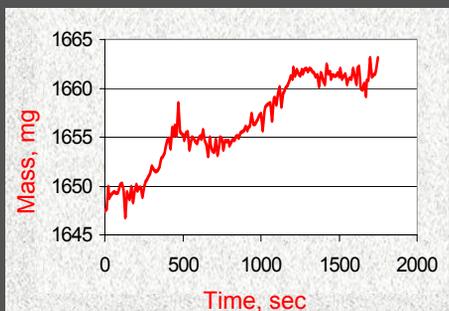
# HP-TGA Data



Conditions represent those attainable at a depth of approximately 500 m, typical of a shallow gas well.

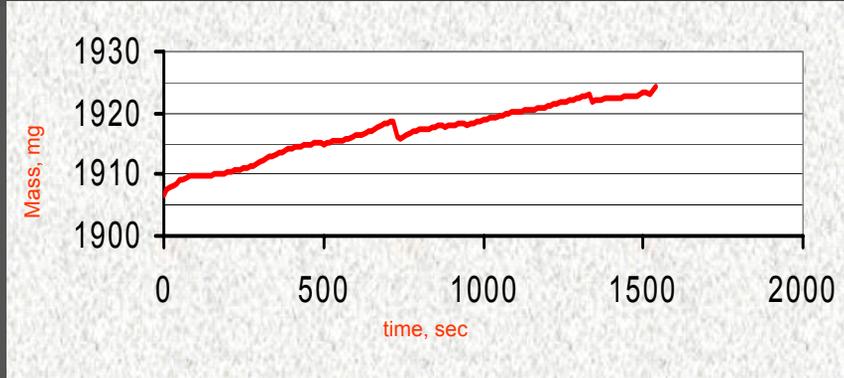
Conditions: 600 psi, 35°C, 30 min

Carbonate formation accounts for a 1.0% increase by weight



# HP-TGA Data

Conditions: 300 psi, 55°C, 25 min



Carbonate formation accounts for a 0.9% increase by weight

# HP-TGA Data

Weight Uptake of the Brine

Uptake observed through direct measurement		Uptake observed through HP-TGA measurement	
Overall increase wt%	Increase to solids wt%	Overall Increase wt%	Increase to solids wt%
1.1	6.5	0.9	5.3

## Conclusions

- The large estimated storage capacity for CO<sub>2</sub> in geologic formations, namely deep brine formations, warrants an investigation into the kinetics of the carbonate forming reactions.
- The uptake of CO<sub>2</sub> into a Pennsylvanian gas well brine can be monitored using high pressure thermo-gravimetric analysis.
- A process for determining a better understanding of the kinetics of formation of mineral carbonates through the sequestration of CO<sub>2</sub> exists through the use of high-pressure thermo-gravimetric analysis.

## References

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