A&WMA 96th ANNUAL CONFERENCE & EXPOSITION

2003 CRITICAL REVIEW

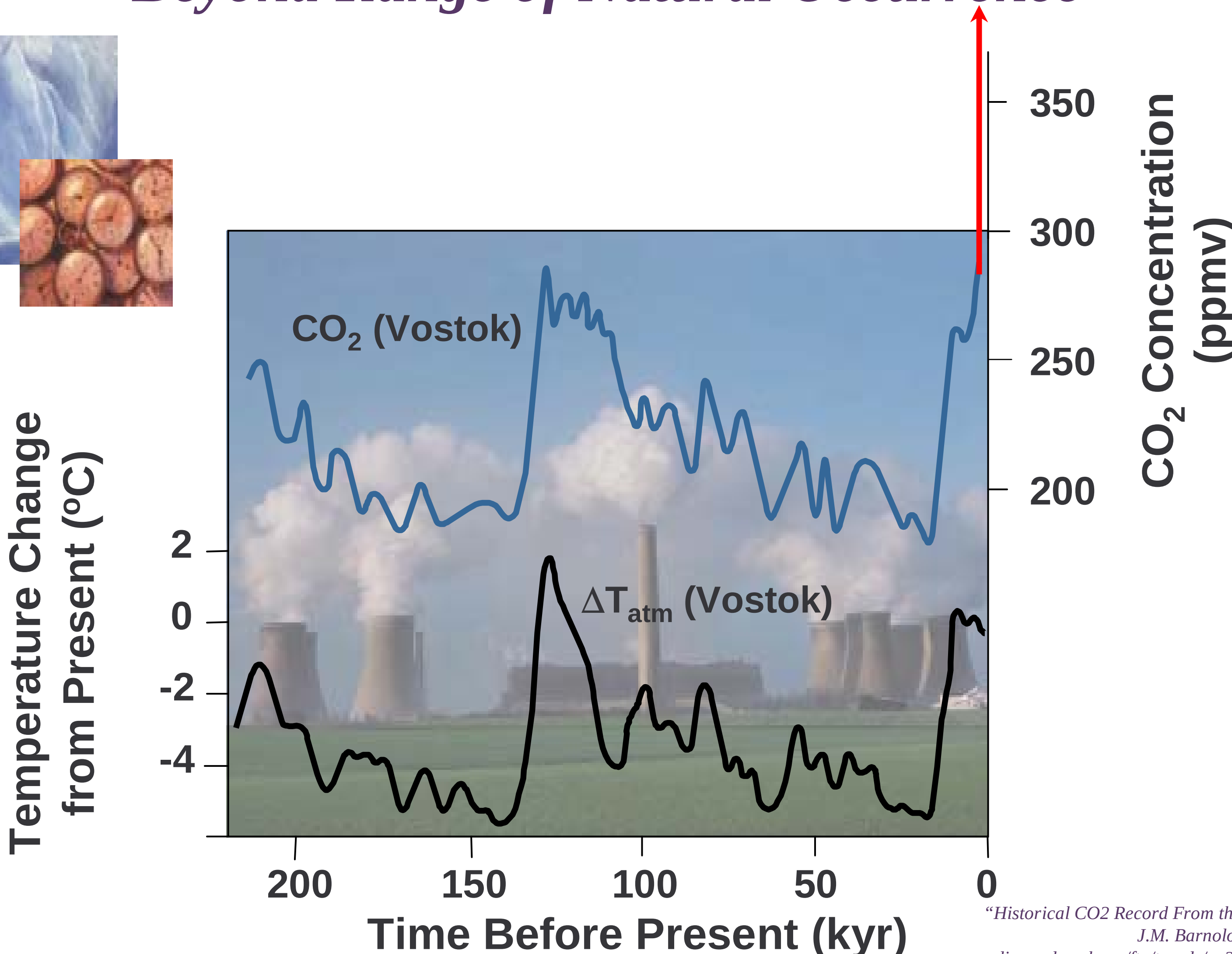
Separation and Capture Of CO_2 From Large Stationary Sources, and Sequestration in Geological Formations -- Coalbeds and Deep Saline Aquifers

Curt M. White

Carbon Sequestration Science Focus Area Leader

JUNE 25, 2003

Global CO_2 Concentrations
Beyond Range of Natural Occurrence



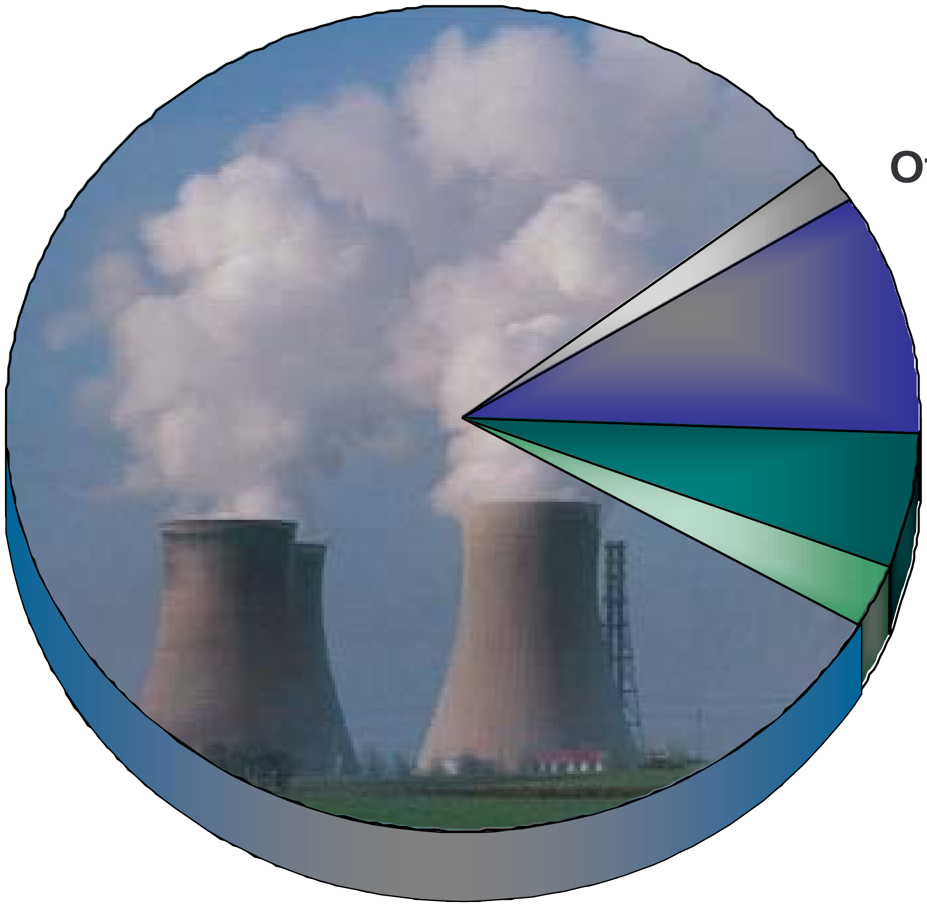
"Historical CO2 Record From the Vostok Ice Core"
J.M. Barnolo et al, August 1999
www.cdiac.esd.ornl.gov/ftp/trends/co2/vostok.icecore.co2

So What's The Problem?

CO_2 & CH_4 - The Primary GHG Contributors

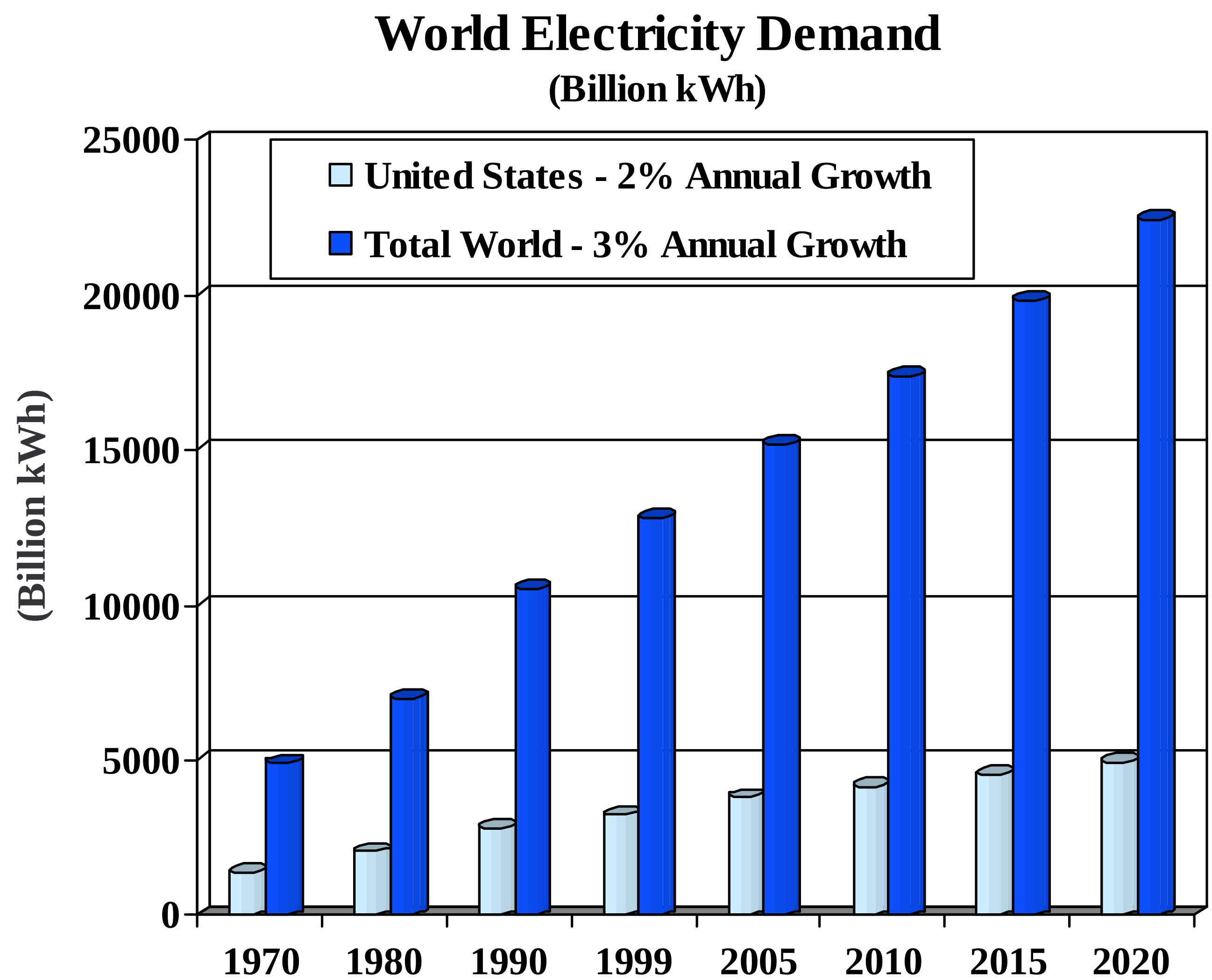
United States Greenhouse Gas Emissions

(Equivalent Global Warming Basis)



"EIA Emissions of Greenhouse Gases in the U.S.: 2000"

GHG Emission Will Continue To Grow



Source: EIA International Energy Outlook 2002

Four Options For Stabilizing Atmosphere CO_2 Concentration

1. **Increasing Energy Efficiency**

   A. More efficient electrical power generating stations[1]

   Average global efficiency of fossil fuel power plants = 31%

State-of-the-Art PC power plant	= 46%	3.7c/KWh
with CO_2 Capture	= 33%	6.4c/KWh
State-of-the-Art NGCC	= 56%	2.2c/KWh
with CO_2 Capture	= 47%	3.2c/KWh
State-of-the-Art IGCC	= 44%	3.8c/KWh
with CO_2 Capture	= 37%	4.9c/KWh

   B. More efficient utilization

2. **Increased Conservation**

3. **Switching to less carbon intensive sources of energy**

   CH_4, renewables (wind, solar, hydroelectric, biomass), nuclear

4. **Carbon sequestration**

   Capture of CO_2 from large stationary sources and storage in the geosphere

[1]*Greenhouse Issues* **2000**, Issue 51, P3.

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Presidential Direction

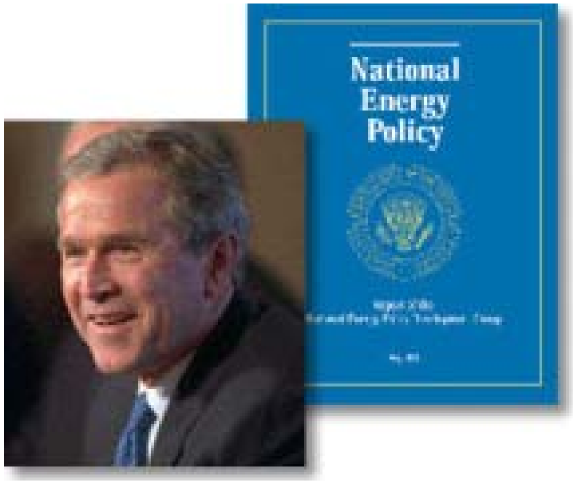
Current Drivers for Carbon Sequestration Program

NCCTI
June 11, 2001

- Third option for global climate change
- Enables continued use of domestic energy resources and infrastructure
- Geologic formations have potential for essentially unlimited storage capacity
- Demonstrated industry interest, participation, and cost-sharing in public/private partnerships
- "We all believe technology offers great promise to significantly reduce emissions -- especially carbon capture, storage and sequestration technologies."

GCCI
February 14, 2002

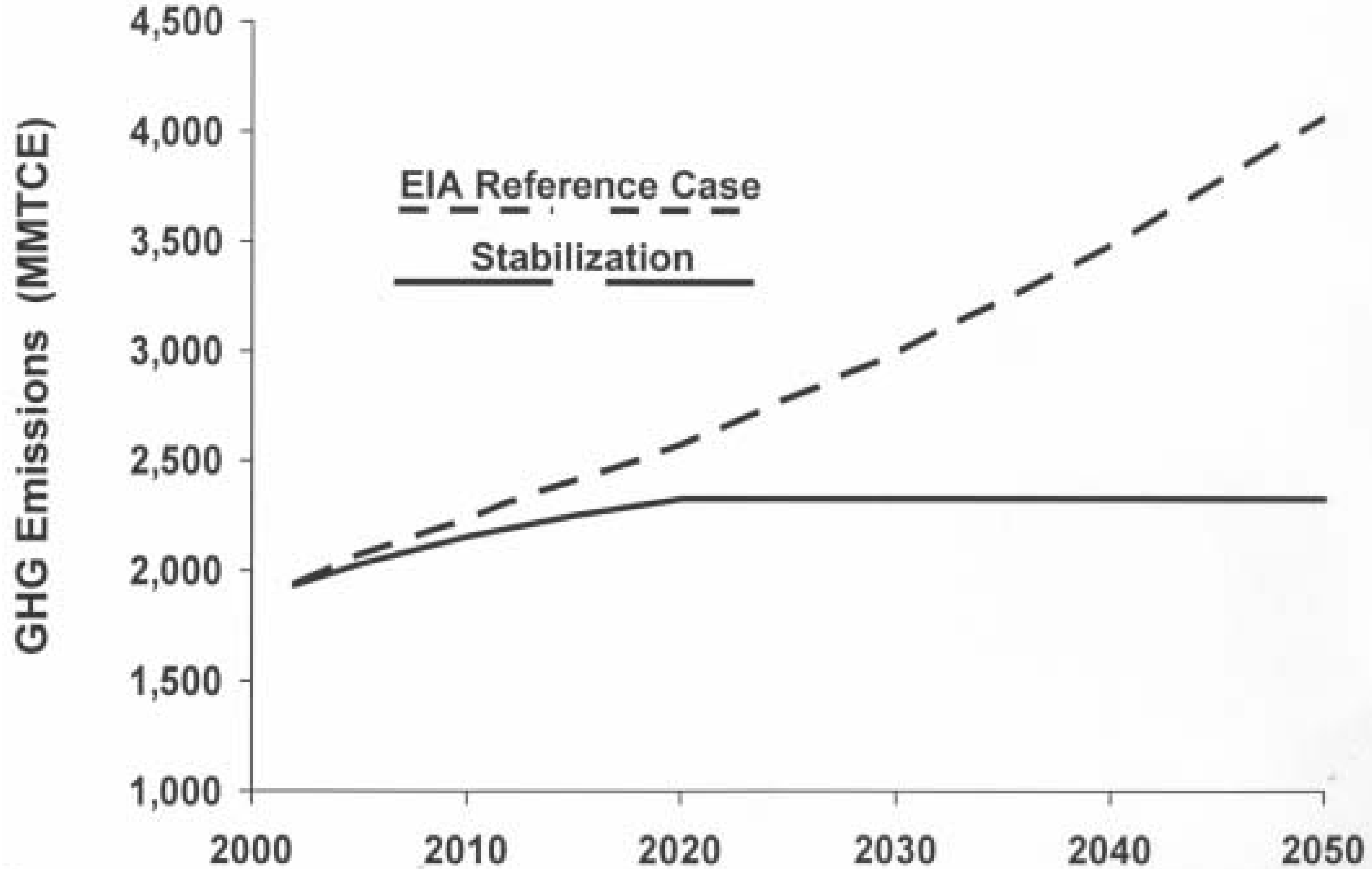
- Sustain economic growth
- Reduce GHG intensity by 18% in next 10 years
- Reevaluate science & path in 2012



White House photo: Paul Morse

Plausible Pathway to Carbon Stabilization

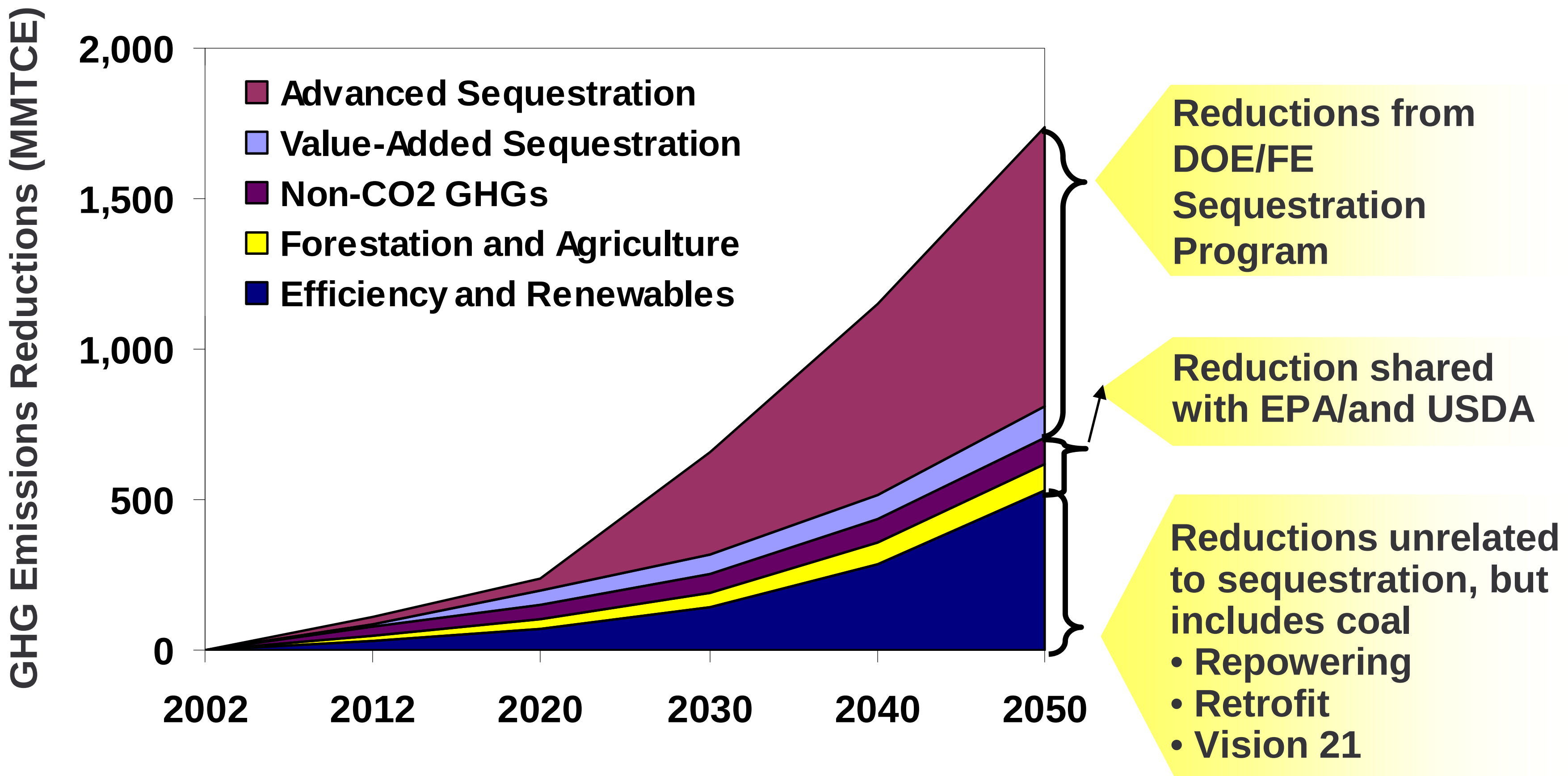
A Significant Undertaking



Klara, S.; Beecy, D.; Kuuskraa, V.; Dipietro, P. Economic Benefits of a Technology Strategy and R&D Program In Carbon Sequestration, *GHT-6*, Kyoto, **2002**.

Sequestration = Stabilization

Could Account For > 60% of Reduction Gap in 2050



Klara, S.; Beecy, D.; Kuuskraa, V.; Dipietro, P. Economic Benefits of a Technology Strategy and R&D Program In Carbon Sequestration, *GHT-6*, Kyoto, **2002**.

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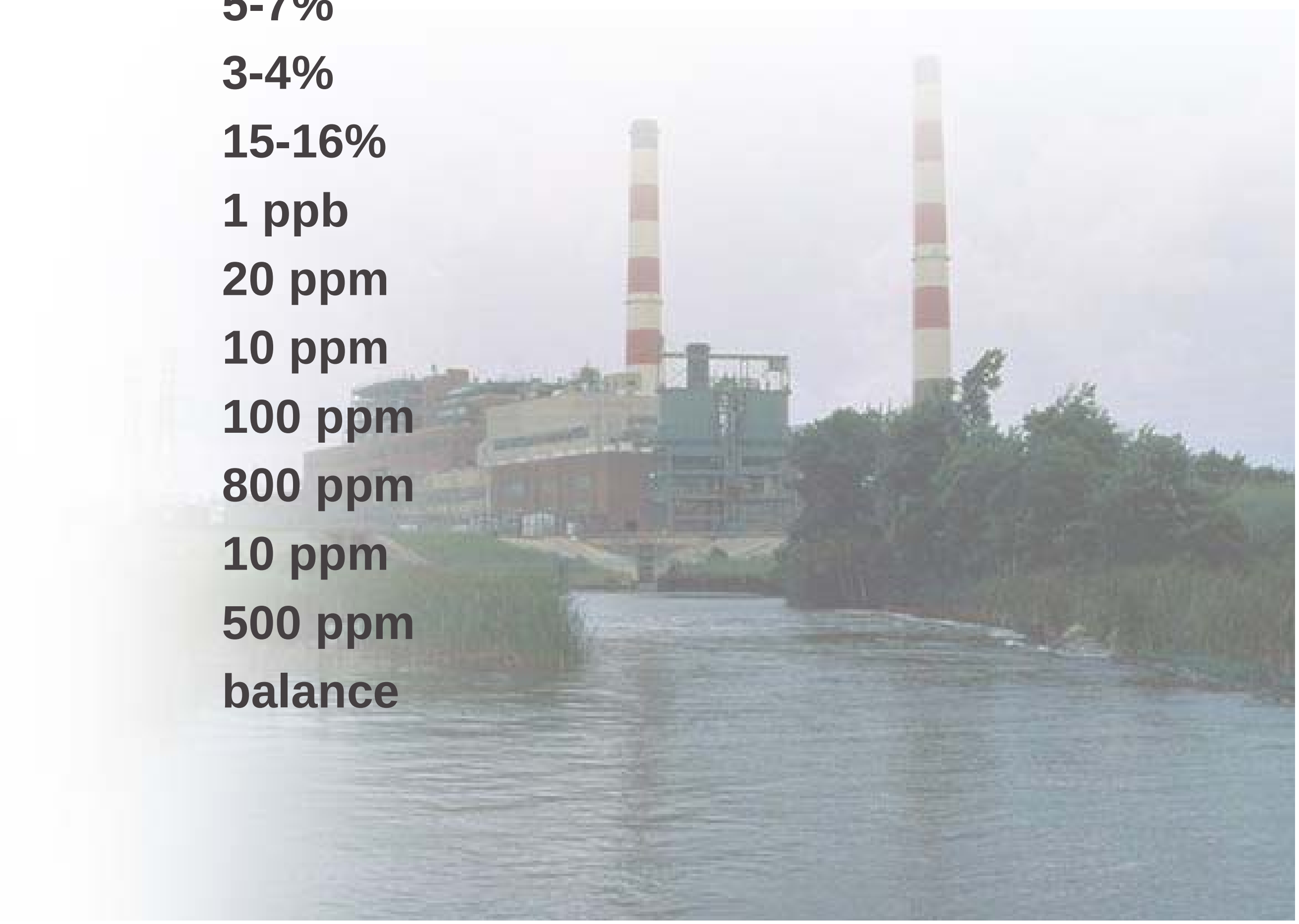
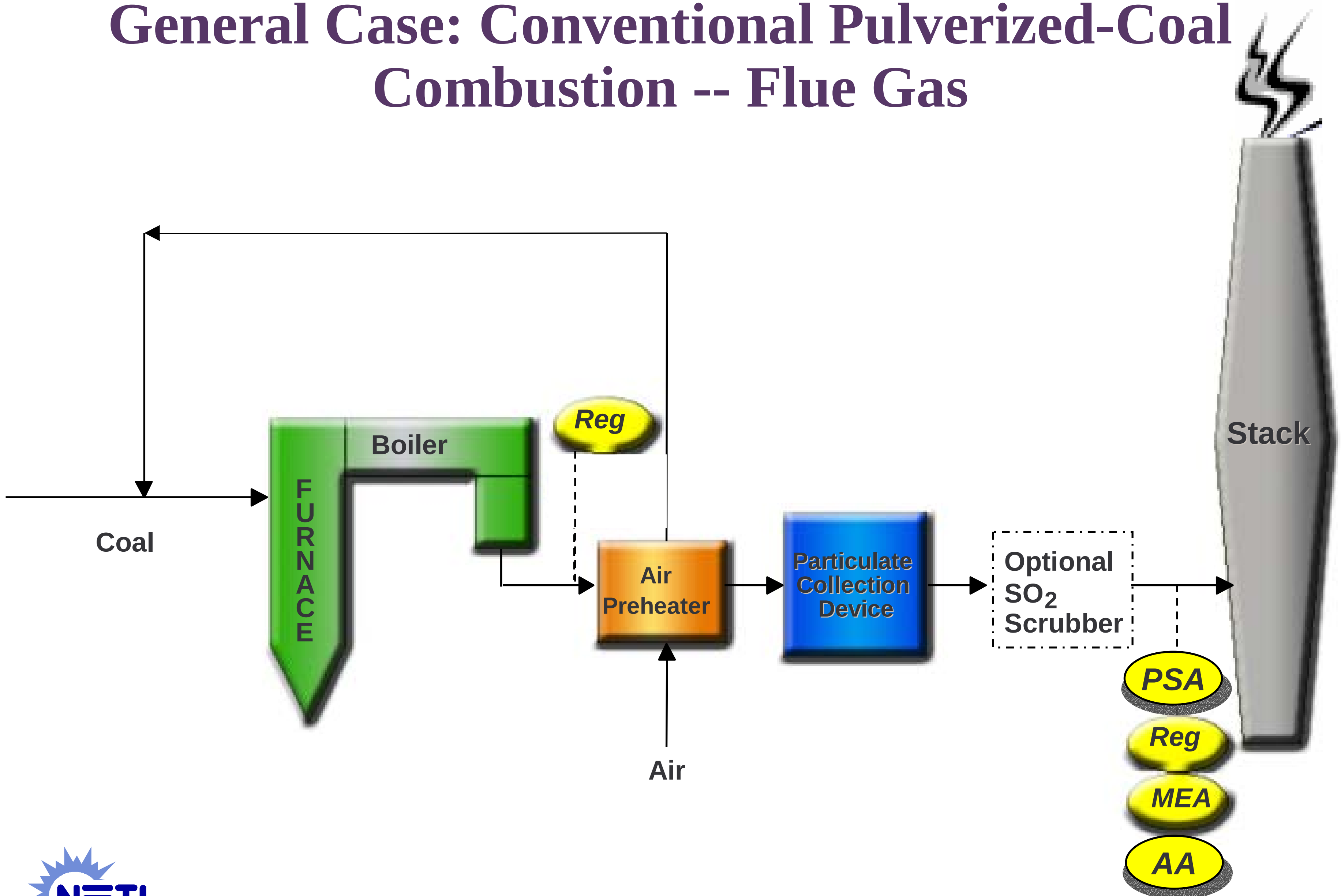
CO_2 SEPARATION AND CAPTURE FROM FLUE GAS AND FUEL GAS

TYPICAL UNTREATED FLUE GAS COMPOSITION

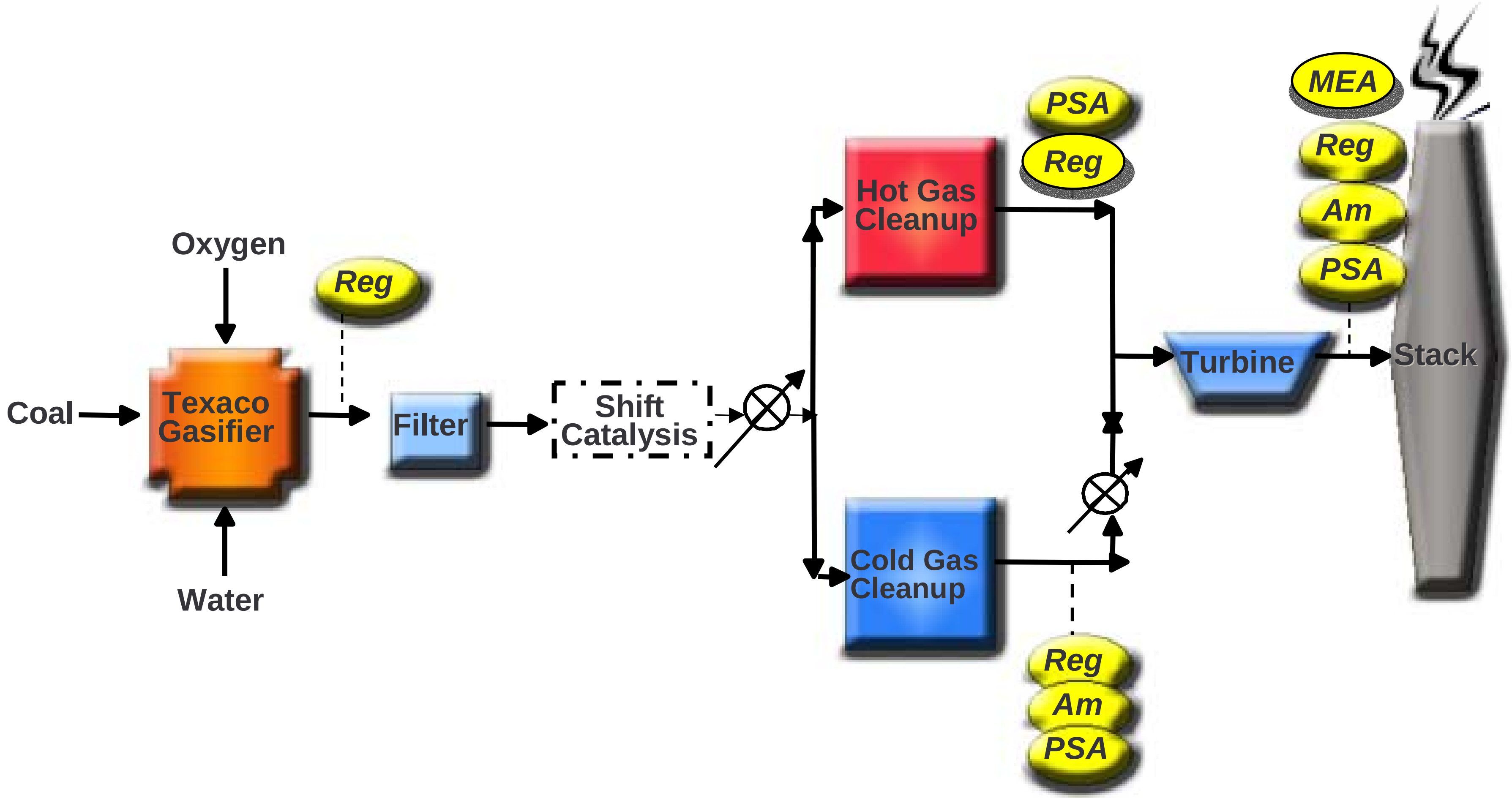
Species	Concentration (by volume)
H_2O	5-7%
O_2	3-4%
CO_2	15-16%
Total Hg	1 ppb
CO	20 ppm
Hydrocarbons	10 ppm
HCl	100 ppm
SO_2	800 ppm
SO_3	10 ppm
NO_X	500 ppm
N_2	balance



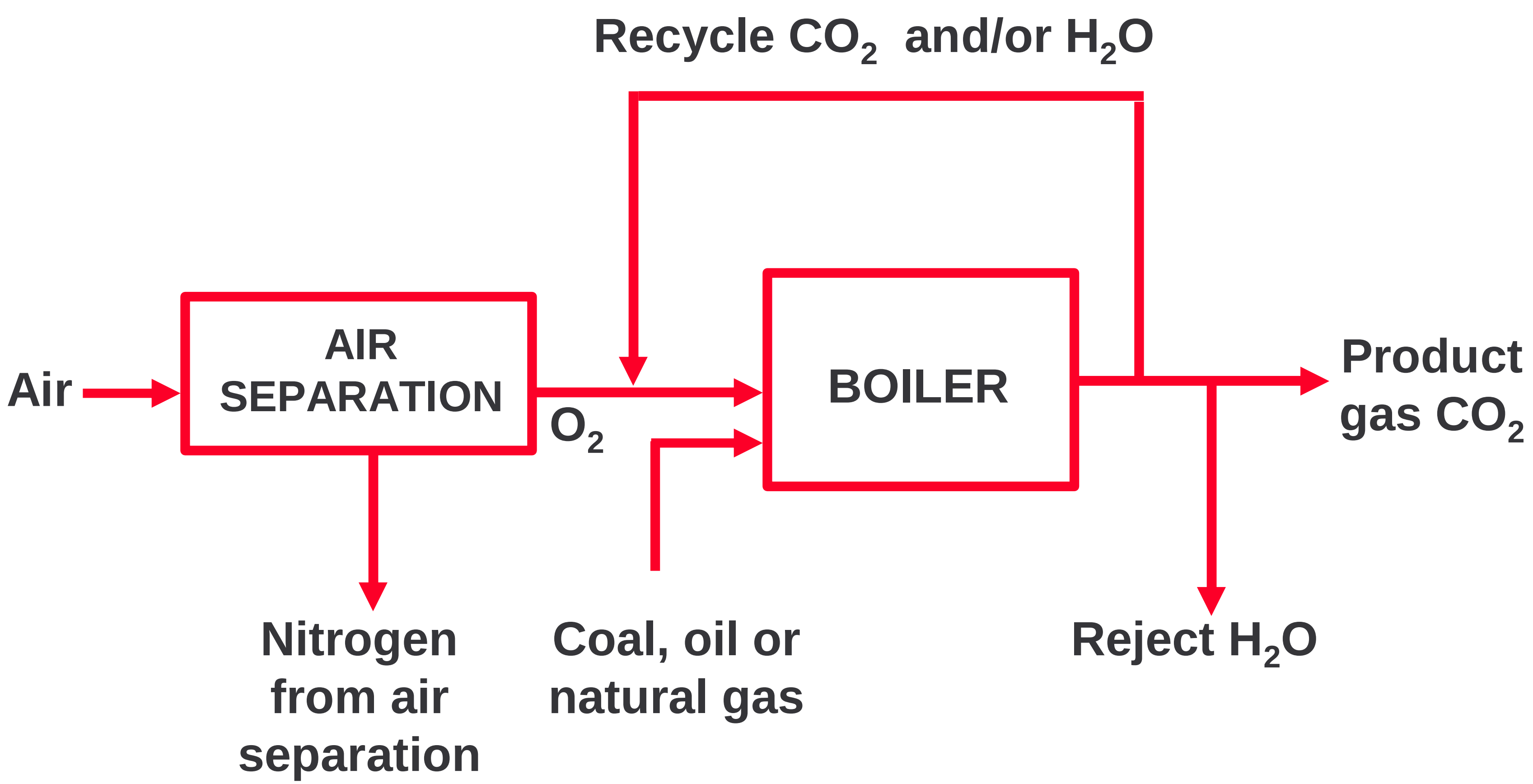
General Case: Conventional Pulverized-Coal Combustion -- Flue Gas



General Case: Advanced Gasification/ IGCC -- Fuel (Synthesis) Gas



O_2/CO_2 Recycle Combustion



General Capture Issues Related To Carbon Sequestration

- **Impact of other pollutants on capture technology**
  - SO_2, NO_X, Hg, and particulates impact the capture technology, dictating where it is applied and what other capture technologies are applied in concert with it.
- **Composition of final capture product and impact on capture/sequestration interface (CO_2 purity, content of other major/minor components)**
  - CO_2 pipelines have strict specifications on the water content of the CO_2.
  - Effect of SO_2, NO_x, and NH_3 on CO_2 pipelines are not well defined.
- **Quantity of CO_2 captured**
  - Millions of tons of CO_2 captured at a single plant dictate very large equipment size.
  - 100% CO_2 capture may not be necessary

The last weld to the CO_2 pipeline is completed near Estavan, Saskatchewan, in December 1999.

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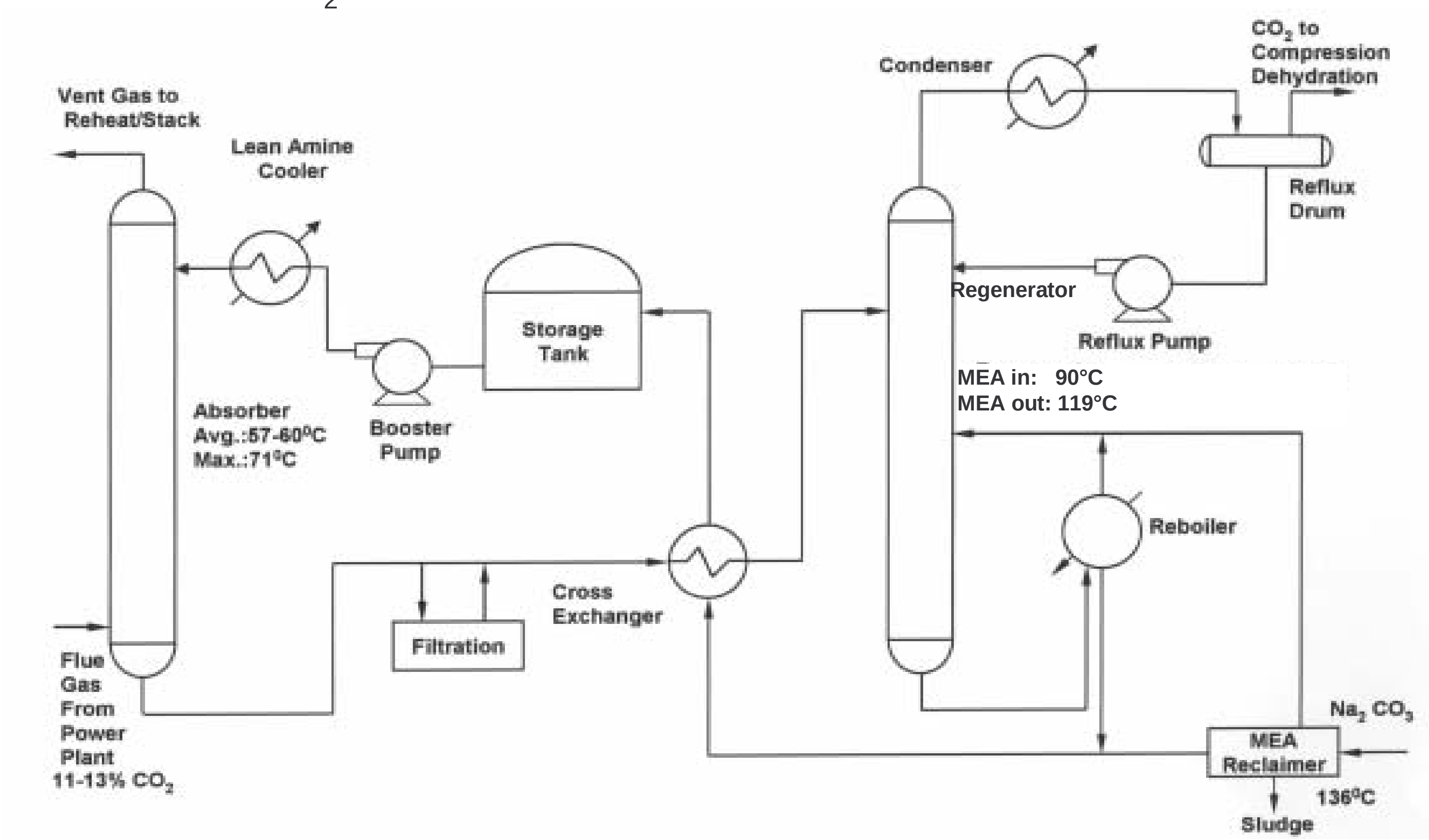
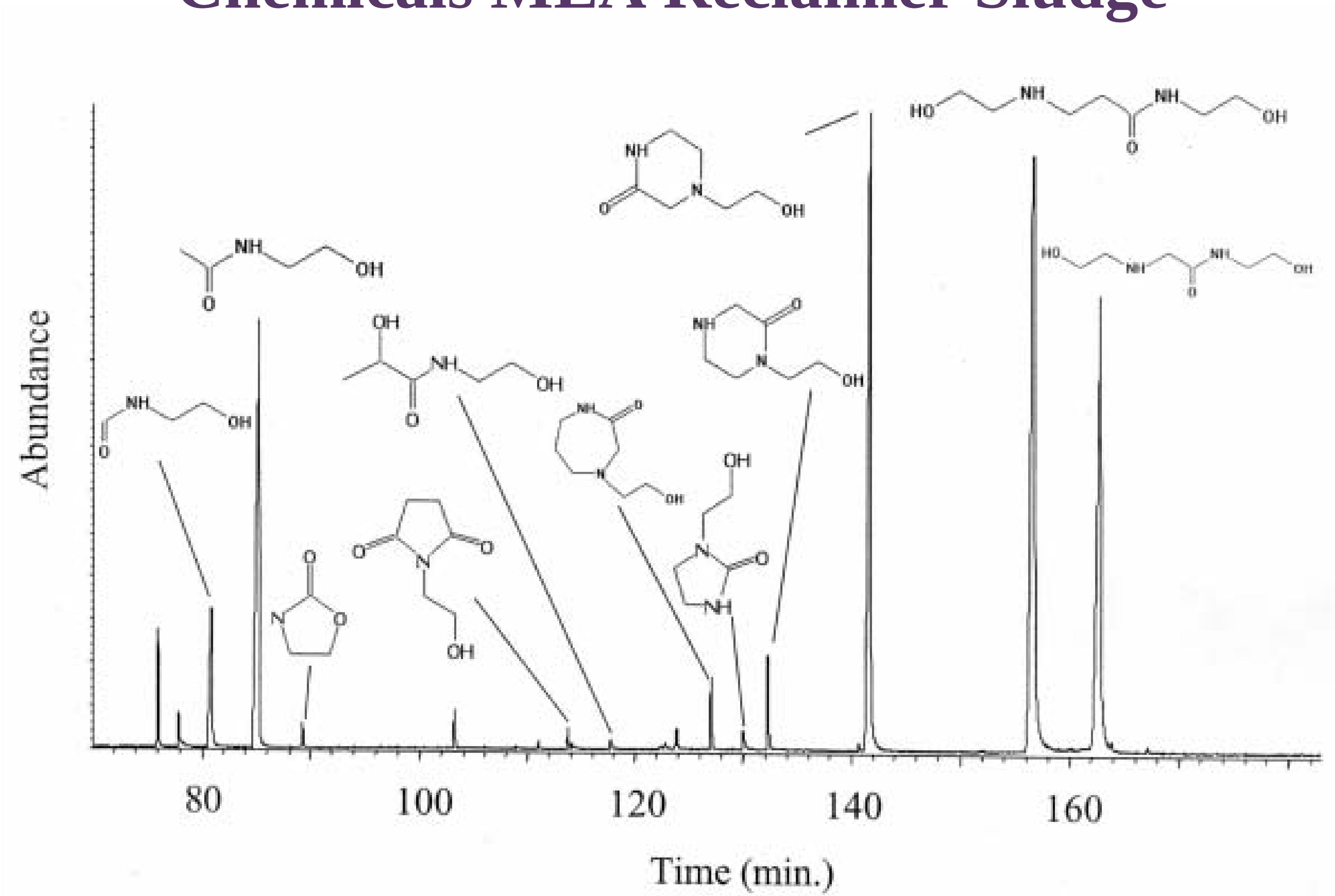
Process Flow Diagram of an MEA CO_2 Capture Plant

$$2CO_2 + 2\underset{\displaystyle OH}{\underset{|}{CH_2}}\text{–}\underset{\displaystyle NH_2}{\underset{|}{CH_2}} + H_2O \rightleftharpoons \underset{\displaystyle OH}{\underset{|}{CH_2}}\text{–}CH_2\text{–}NHCO_2^- + \underset{\displaystyle OH}{\underset{|}{CH_2}}\text{–}CH_2\text{–}NH_3^+ + H_2CO_3$$



Herzog, H.; Golomb, D.; Zemba, S., Feasibility, Modeling and Economics of Sequestering Power Plant CO_2 Emissions in the Deep Ocean, *Environ. Prog*. **1991**, 10, 64-74

MEA Degradation Products From The IMC Chemicals MEA Reclaimer Sludge



Strazisar, B.; Anderson, R. R.; White, C. M., Degradation Pathways for Monoethanolamine In a CO_2 Capture Facility, *Energy & Fuels* **2003,** in Press**.**

TYPES OF CAPTURE PROCESSES

- **Solvents--Wet Scrubbing**
  - Chemical solvents – chemical reaction between CO_2 and the solvent. The MEA process is an example
  - useful for flue gas applications
  - favored by low concentrations of CO_2 in the gas stream and ambient pressure operation
  - four commercial plants in the U.S. using MEA
  - experimental – Aqua Ammonia Process

Warrior Run CO_2 Capture Plant

IMC Chemicals CO_2 Capture Plant

Solvents--Wet Scrubbing

- physical solvents – CO_2 selectively dissolves in the solvent usually under high pressure. The Selexol, Rectisol and Morphysorb processes are examples
- useful for fuel gas applications
- favored by high pressure operations and high concentrations of CO_2 in the gas stream
- one commercial scale gasification plant, Dakota Gasification, produces 6.8 million standard m^3 per day of dry CO_2 – 96% CO_2, 1% H_2S, 3% hydrocarbons, 330 km pipeline to Weyburn oilfield, 18.16 MPa

Courtesy of Dakota Gasification

Picture of CO_2 pipeline installation

Dry Regenerable Sorbents

– Solid Chemical Absorption – Reaction between sorbents and CO_2

$$M_2CO_3 + CO_2 + H_20 \rightleftharpoons 2MHCO_3$$

M = Li, Na, K ect.

- Experimental processes only – RTI Na_2CO_3 for flue gas

$$MO + CO_2 \rightleftharpoons MCO_3$$

M = Mg, Ca, ect.

- Experimental processes only – OSU CaRS-CO_2 process for fuel gas

$$Li_4SiO_4 + CO_2 \rightleftharpoons Li_2SiO_3 + Li_2CO_3$$

$$Li_2SiO_3 + CO_2 \rightleftharpoons Li_2CO_3 + SiO_2$$

$$Li_4SiO_4 + 2CO_2 \rightleftharpoons 2Li_2CO_3 + SiO_2$$

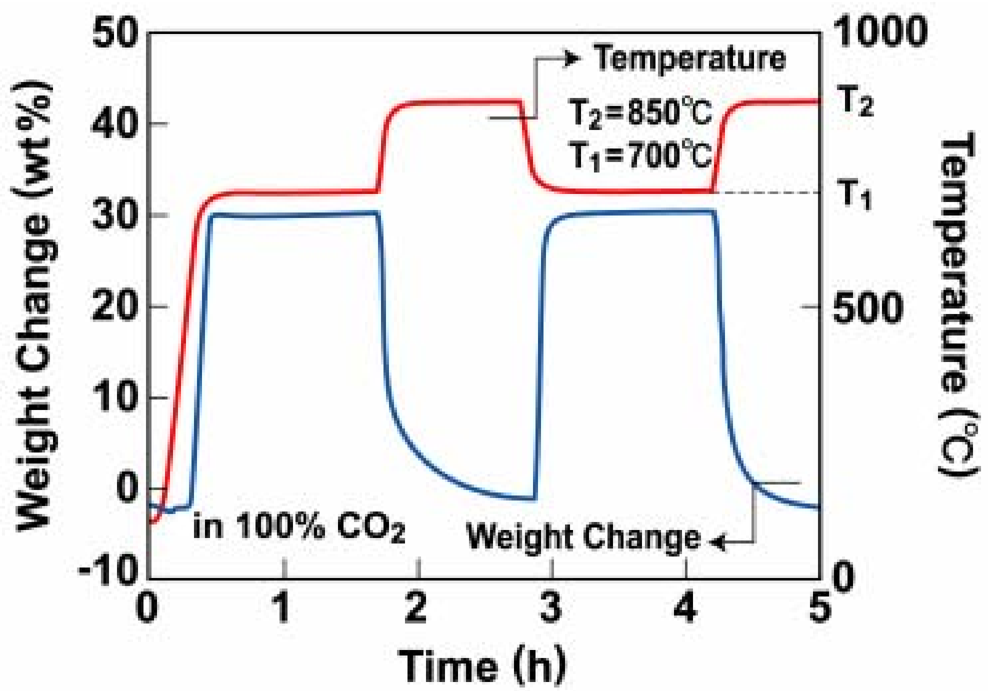
- Experimental process only – Toshiba useful for both flue and fuel gas

Properties of lithium silicate

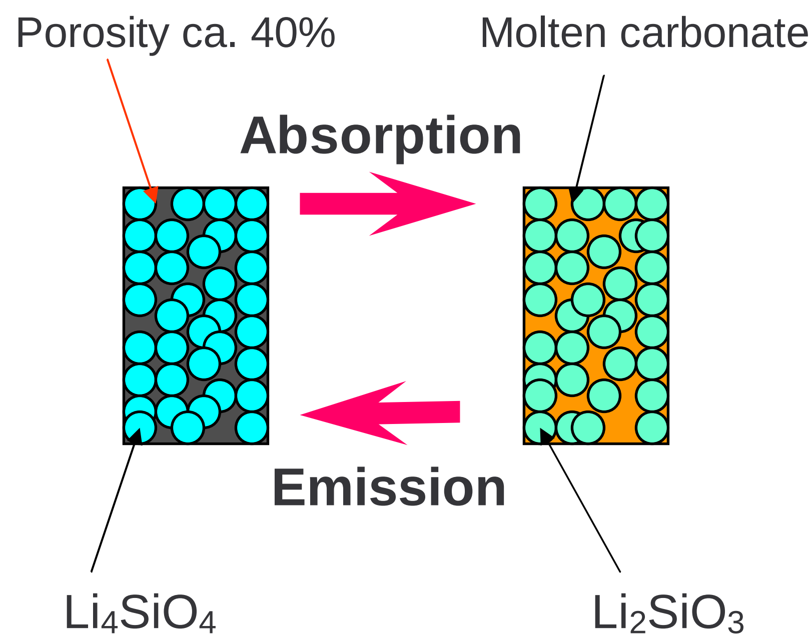
	Density	2.4g/cm^3
	Crystal Structure	Monoclinic
	Particle Diameter	1-5 micron (ca. 1m^2/g)
	Color	White
Absorbent		Porous bodies with ca. 40% of porosity. Cylindrical pellets and granulated powder are possible

Cyclic TGA Study (1-1)

Cyclic behavior of absorption and emission



Porous Absorbent



Dry Regenerable Sorbents

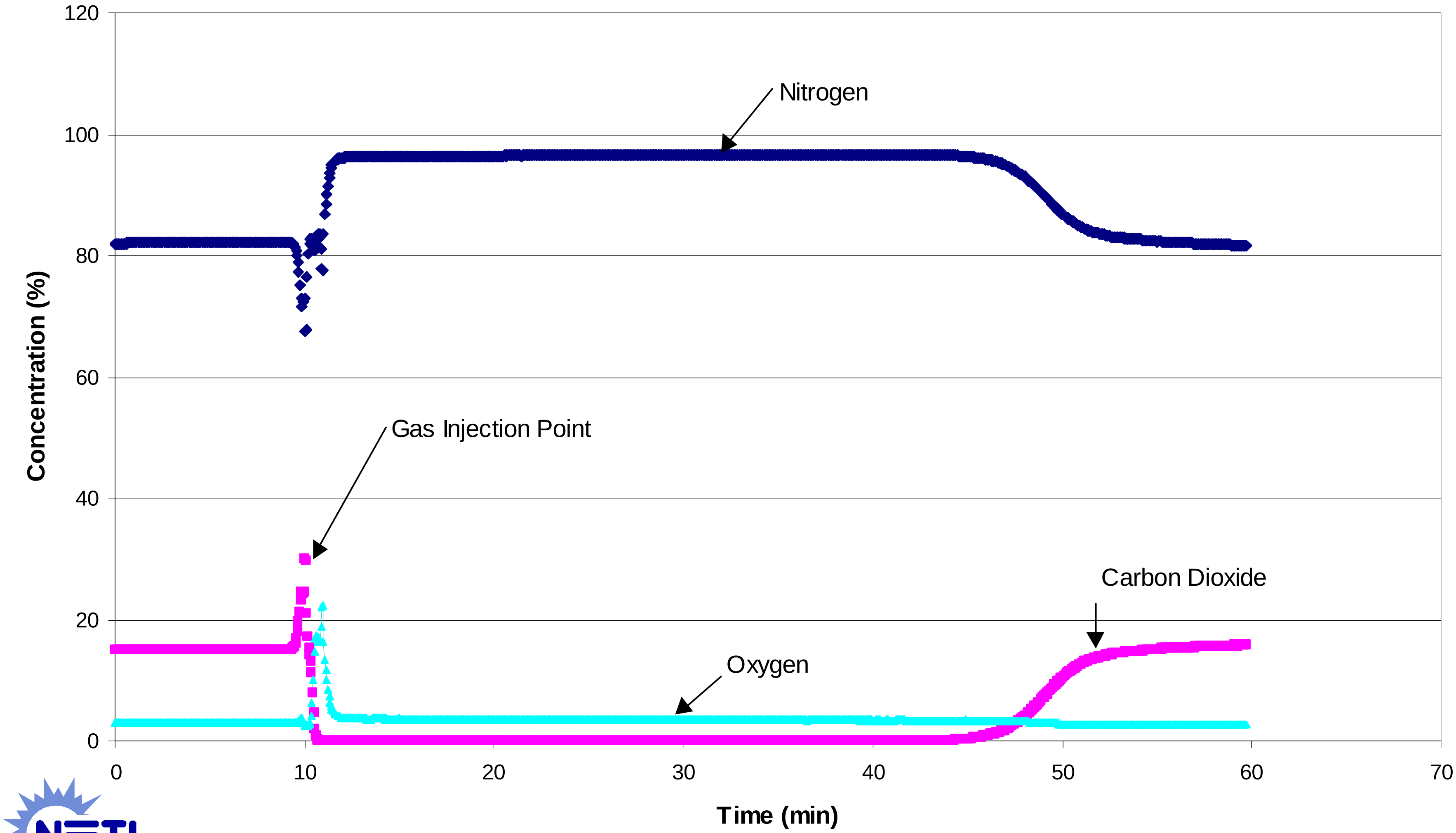
- Physical adsorption – Pressure (PSA) or Temperature Swing Adsorption (TSA). CO_2 is selectively adsorbed by a solid such as molecular sieves or activated carbon
- Useful for flue gas and fuel gas applications
- IEA study concluded it was energy intensive and expensive

  PSA CO_2 adsorbed at high pressure – desorbed at low pressure

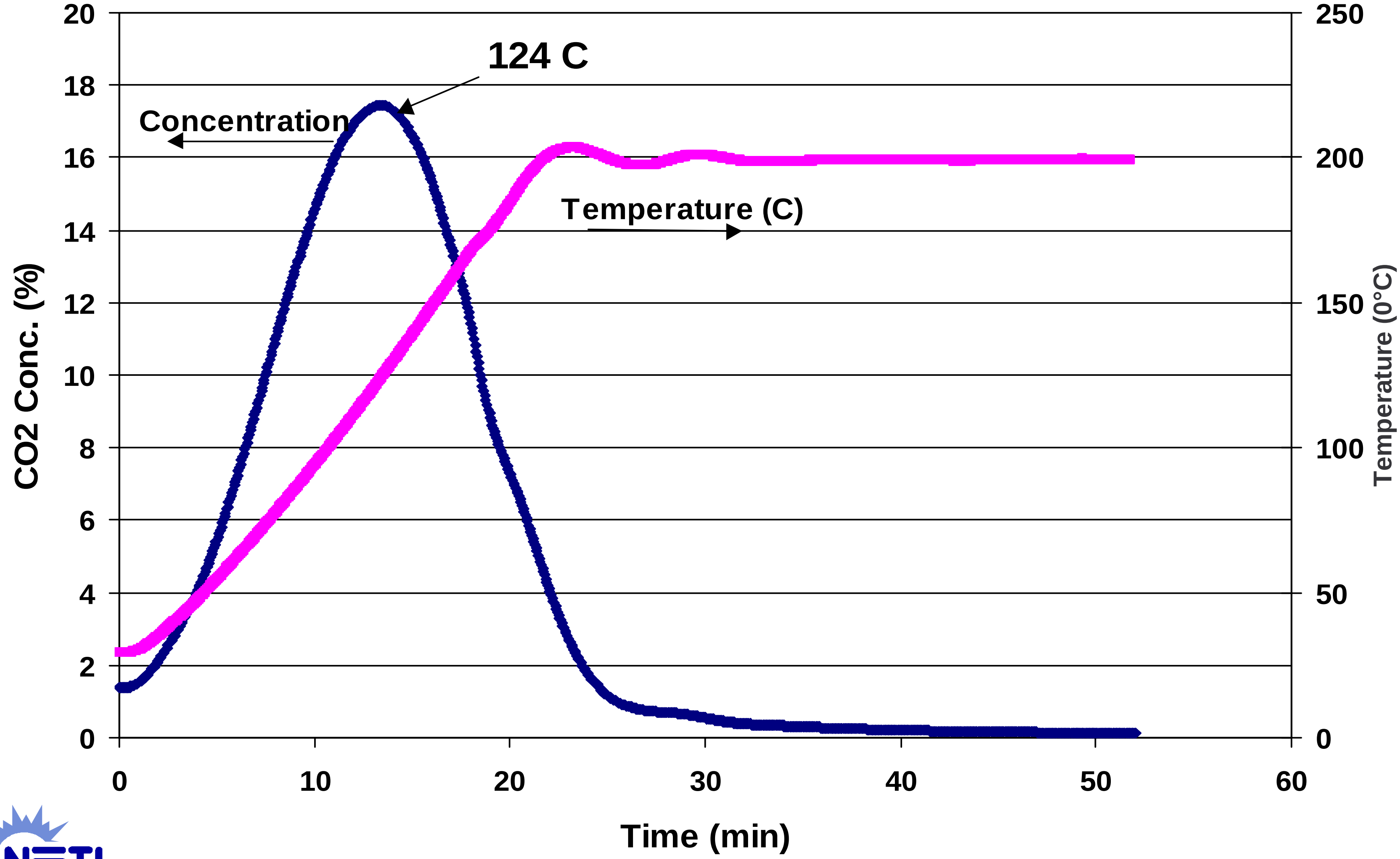
  TSA CO_2 adsorbed at low temperature – desorbed at high temperature

- Experimental – combination of PSA and TSA has been tested at the pilot scale with 1000 m^3/h flue gas at Yokosuka Thermal Power Station in a 2000h test.
  - Promising results
  - CO_2 enriched to 99% with CO_2 recovery at 90%
- Activated carbons
- Aminated sorbents

Adsorption of CO_2, N_2, and O_2 on Molecular Sieve 13X (15% CO_2, 3%O_2, 82% N_2, and saturated with water vapor at 25 C, 15 cc/min, in Atmospheric Reactor)

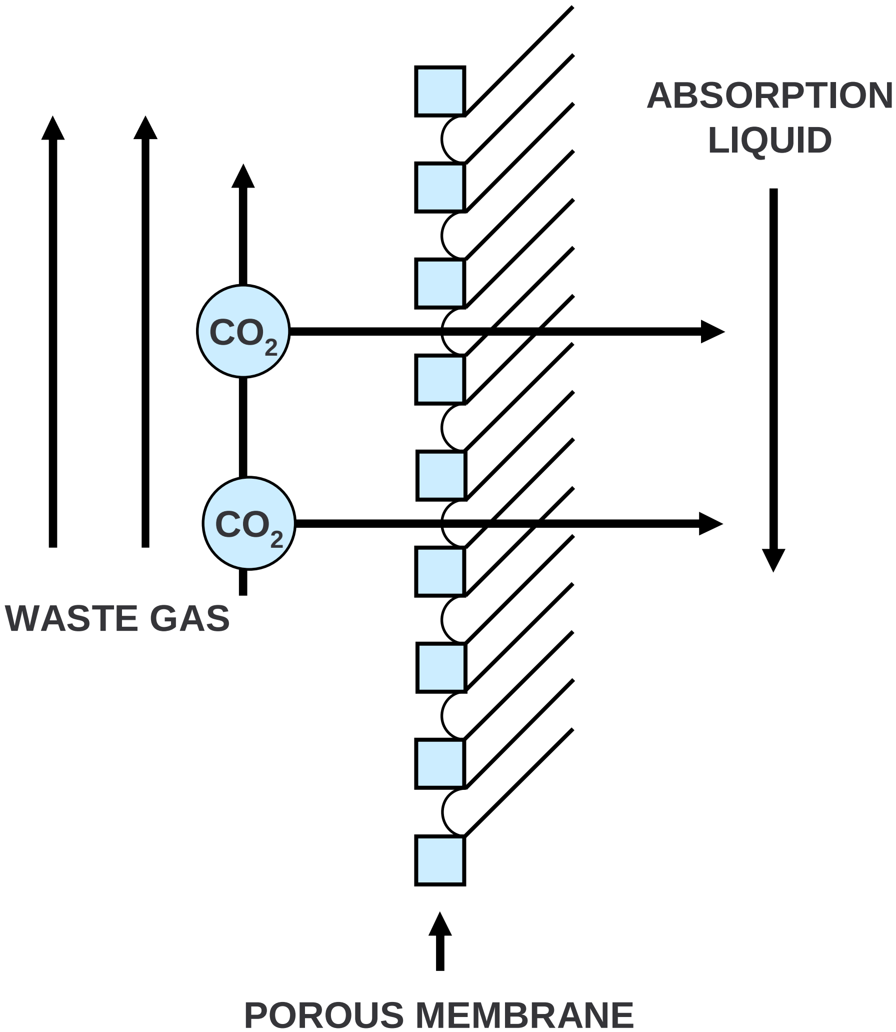


Temperature Programmed Desorption Studies with Zeolite 13X after CO_2 Adsorption



Membranes – Allow the Selective Transport or Selective Exclusion of CO_2 Through a Barrier

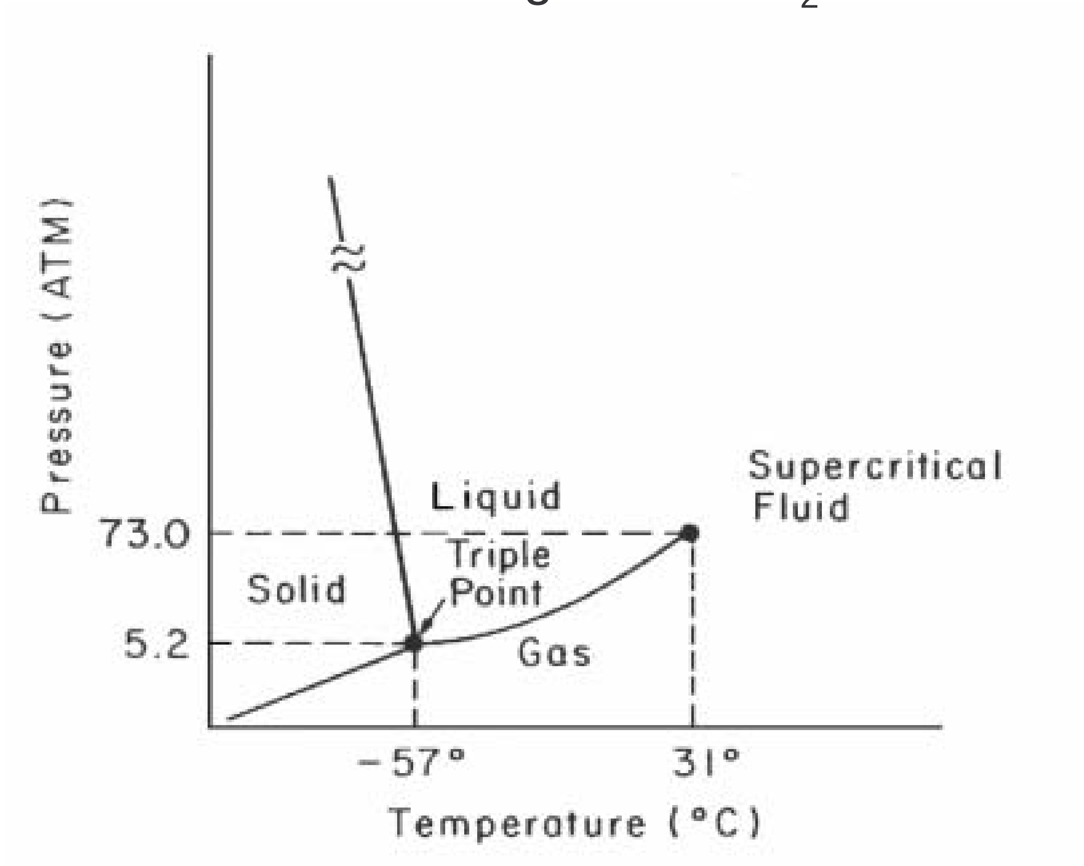
- Useful for flue gas and fuel gas applications
- Membrane separation processes often require less maintenance and energy than other methods
- Successfully applied to separation of CO_2 from natural gas
- Experimental development stage



GEOLOGICAL SEQUESTRATION

Fundamental Physical and Chemical Properties of CO_2 that Effect Sequestration in the Geosphere

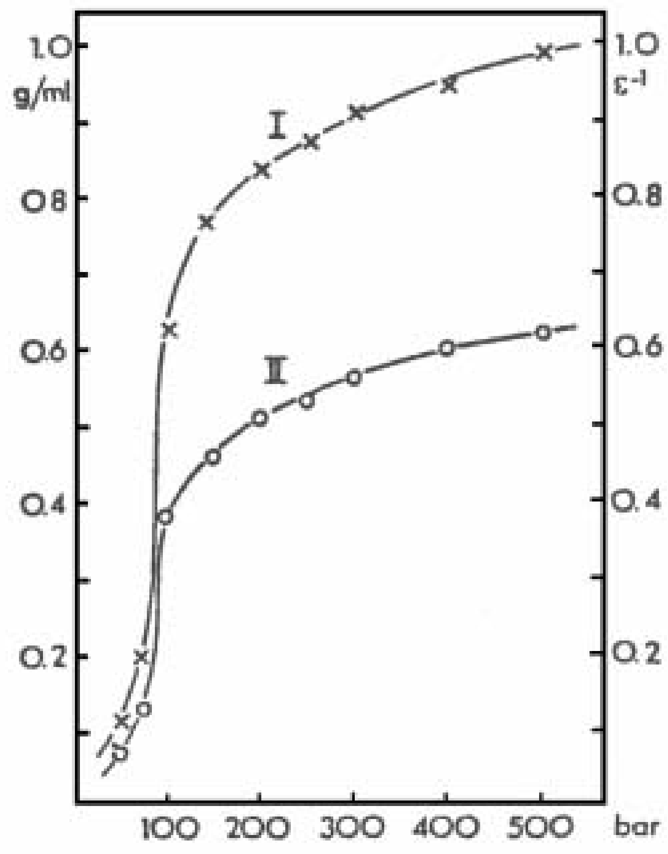
Phase Diagram of CO_2



White, C. M.; Houck, R. K., *J. High Resolution Chromatogr., Chromatogr. Commun.* **1986**, 9, 4-17.

Fundamental Physical and Chemical Properties of CO_2 that Effect Sequestration in the Geosphere

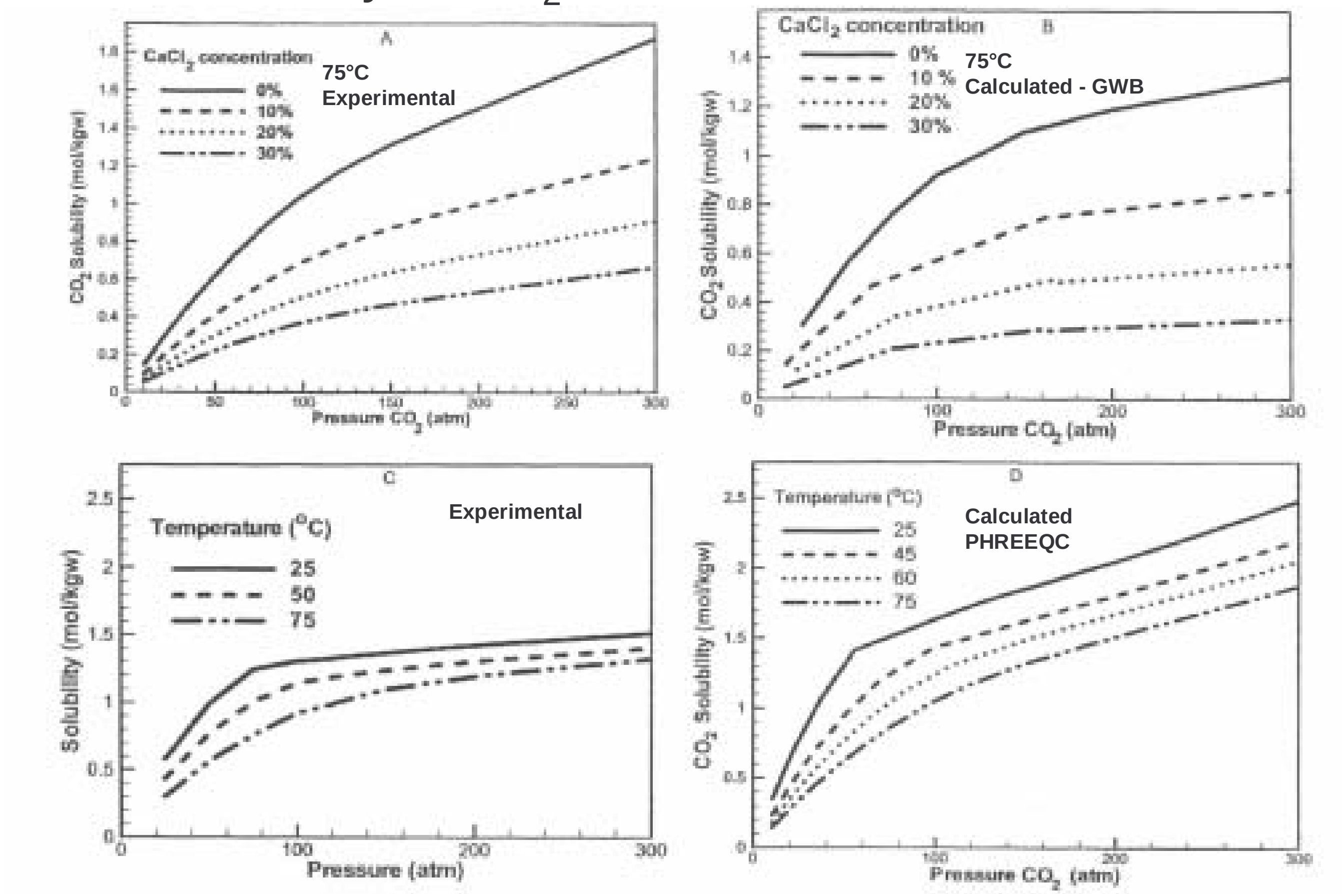
Relationship Between Pressure, Density, and Dielectric Constant



Stahl, E.; Schilz, W.; Shultz, E.; Willing, E., *Angew. Chem. Int. Ed. Engl.* **1978**, 17, 731-738.

Fundamental Physical and Chemical Properties of CO_2 that Effect Sequestration in the Geosphere

Solubility of CO_2 in Pure Water and Brine



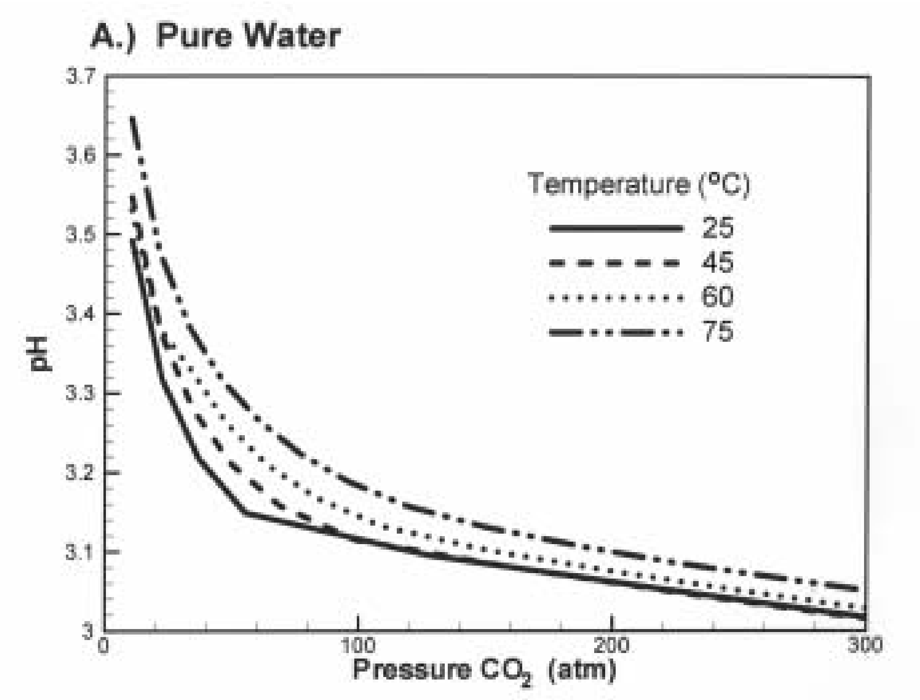
Prutton, C. F.; Savage, R. L., *J. Am. Chem. Soc.* **1945**, 67, 1550-1554.

Wiebe, R.; Gaddy, V. L., *J. Am. Chem*. Soc. **1939**, 61, 315-318.

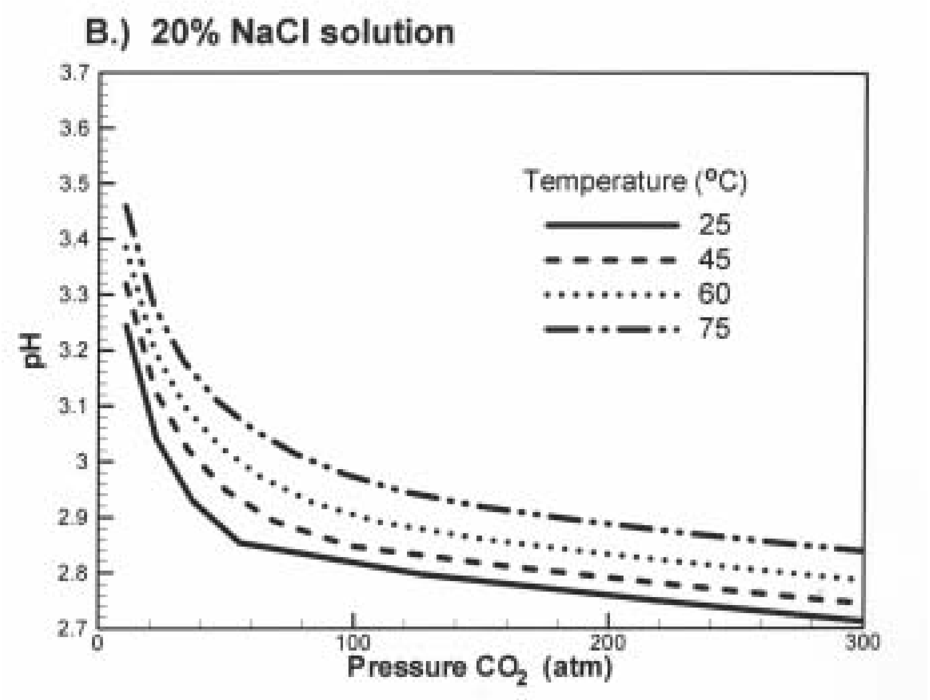
Wiebe, R.; Gaddy, V. L., *J. Am. Chem. Soc.* **1940**, 62, 815-817.

Fundamental Physical and Chemical Properties of CO_2 that Effect Sequestration in the Geosphere

pH of CO_2 in Pure Water and Brine at Various Temperatures and Pressures



PHREEQC



GWB

COAL SEAM SEQUESTRATION

Burlington Resources Coalbed CH_4 Recovery/CO_2 Sequestration Project In The New Mexico San Juan Basin At The Allison unit; Near A CO_2 Pipeline.

4 – Injection wells

9 – Recovery wells

After 5 years, injected 57 million m^3 of CO_2

1 Additional volume of CH_4 produced for 2 Volumes of CO_2 injected

CO_2 Injection Well

CH_4 Recovery Well

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ESTIMATED CO_2 STORAGE CAPACITY OF GASSY COALS

	Gt of CO_2
N. America, Australia and India [1]	37.8
The Netherlands [2]	8
Worldwide [3]	300-964
Worldwide [4]	225

5 -15 Gt of CO_2 sequestered at a profit[4]

60 Gt of CO_2 sequestered at a cost <$50 per ton[4]

150 Gt of CO_2 sequestered at a cost of $100 -$200 per ton[4]

1. Reeves, S. *Seminar at NETL*, **2001.**
2. Hamelinck, C. N.et al., Potential for CO_2 Sequestration and Enhanced Coalbed Methane Production in the Netherlands, Novem report www.chem.uu.nl.
3. Gunter. W. D. ; Wong, S.; Cheel, D. B.; Sjostrom, G., *Appl. Energy* **1988**, 61, 209-227.
4. Stevens, S. H.; Kuuskraa, V. A.; Spector, D.; Riemer, P., 4th International Conference on GHGT – 4.

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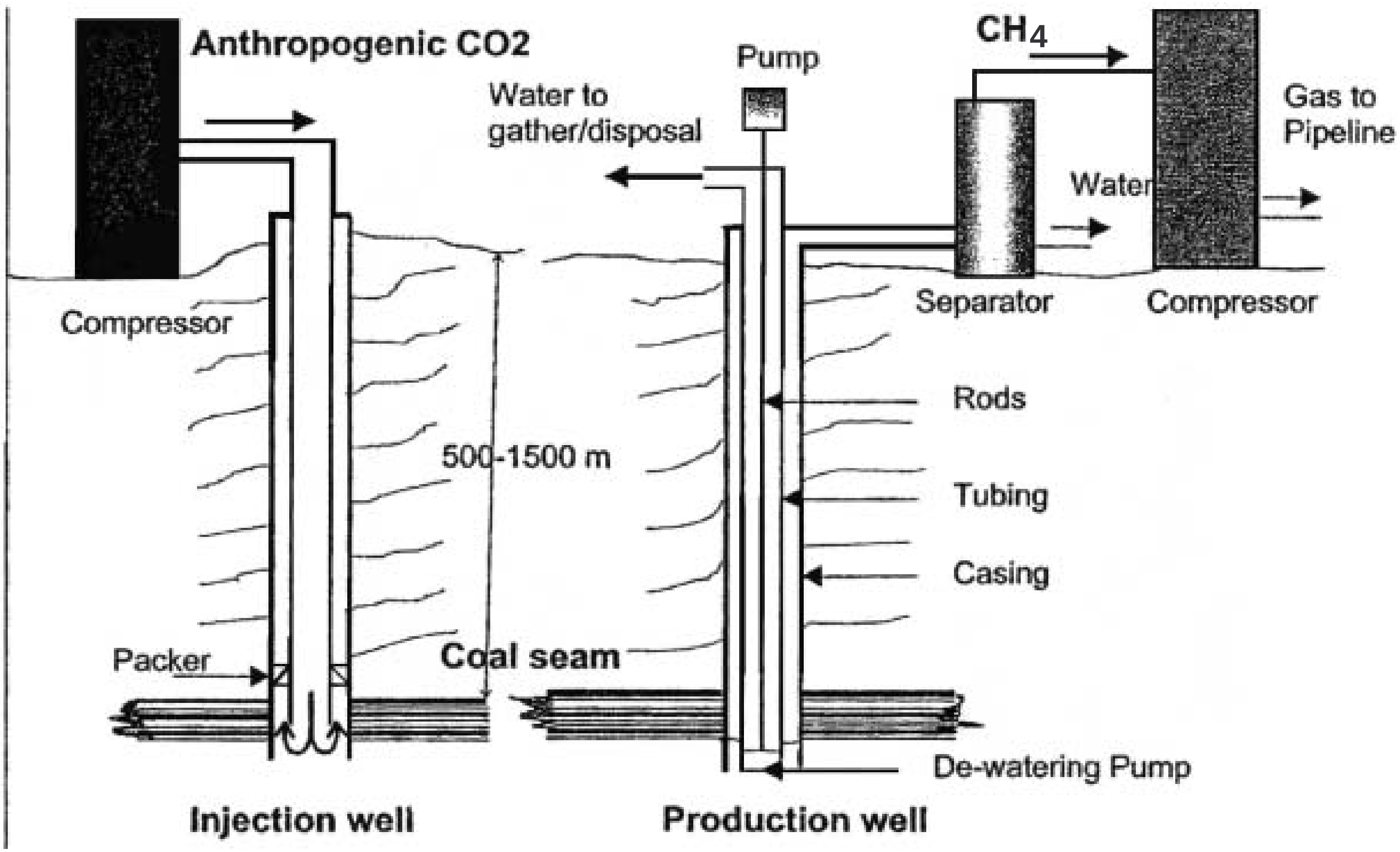
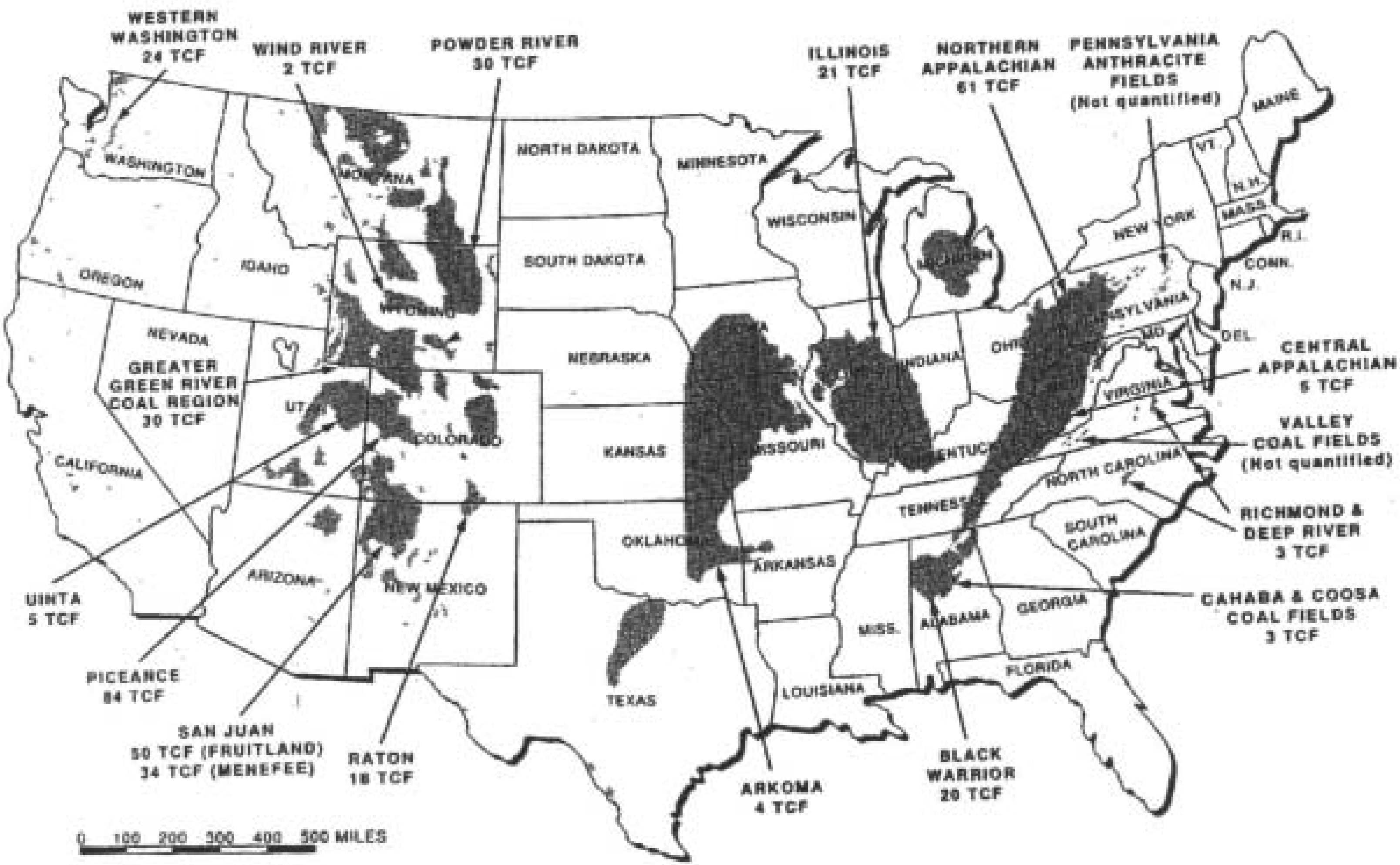
COAL SEAM SEQUESTRATION



MAP OF US COALBED CH_4 DEPOSITS



COAL SEAM SEQUESTRATION

Ranking of World's Most Prospective Coal Deposits for CO_2 Enhanced Coal Bed Methane Recovery/Sequestration for 13 Coal Basins. The ranking scale is 1(lowest) to 5 (highest). The individual rankings for each basin from 1 to 13 are also given along with the estimated amounts of additional CH_4 that can be recovered due to CO_2 injection in Tcf, and the estimated amounts of CO_2 that can be stored in 10^6 tons. [300]

Coal Basin/ Region	Country	Potential Reserves	Resources Concentration	ECBM Producibility	Development Costs	Gas Sales Market	CO_2 Availability	Overall Score	Ranking	CO_2 Enhanced Reserves[a] (Tcf)	CO_2 Sequestration Potential (10^6 t)
San Juan	U.S.A.	5	5	5	5	4	5	29	1	13	1400
Kuznetsk	Russia	5	4	4	3	4	4	24	3	10	1000
Bowen	Australia	5	4	4	4	4	3	24	4	8.3	870
Ordos	China	4	3	4	3	2	2	18	13	6.4	660
Sumatra	Indonesia	4	3	3	3	4	4	21	8	3.5	370
Uinta	U.S.A.	2	3	5	5	4	5	24	2	2.2	230
Western Canada	Canada	4	2	3	4	3	3	19	9	1.6	170
Sydney	Australia	4	4	3	3	4	4	22	7	1.4	150
Raton	U.S.A.	2	3	4	5	4	5	23	5	0.8	90
Cambay	India	3	5	3	4	5	3	23	6	0.7	70
Donetsk	Ukraine/ Russia	1	5	2	3	4	4	19	11	0.3	30
Northeastern China	China	2	4	2	3	4	4	19	12	0.2	20
Damodar Valley	India	2	3	2	4	4	4	19	10	0.1	10
Total of high-potential basins										48.5	5070

Reeves, S., *Seminar at NETL*, **2001**

In any new area of science and technology it is often beneficial to formulate hypotheses and then work toward proving, disproving and refining them.

- HYPOTHESIS --THE GLASS-TO-RUBBER TRANSITION TEMPERATURE (T_g) OF COAL WILL BE REDUCED BY IMBIBITION OF CO_2. THE COAL WILL BECOME PLASTICIZED.
- HYPOTHESIS -- THERE WILL BE A SUBSTANTIAL INCREASE IN THE SELF DIFFUSIVITY OF CO_2 IN COAL ONCE IT HAS BECOME PLASTICIZED AND IS ABOVE ITS T_g.
- HYPOTHESIS -- THE DEGREE TO WHICH PLASTICIZATION, SWELLING, INCREASED DIFFUSIVITY, LOWERING OF T_g, RELAXATION OF THE MACROMOLECULAR NETWORK, AND DEPRESSION OF THE SOFTENING TEMPERATURE OCCUR, WILL BE LIMITED BY THE DEGREE THAT THE COAL IS FREE TO SWELL.
- HYPOTHESIS -- THE DIFFUSIVITY OF CO_2 IN COAL SWOLLEN BY HIGH PRESSURE CO_2 CAN BE DESCRIBED BY FREE VOLUME THEORY.
- HYPOTHESIS --THE CLEAT SYSYTEM WITHIN THE COAL BED WILL BEGIN TO CLOSE AND BECOME RESTRICTED, SLOWING DARCY FLOW WITHIN THAT AREA OF THE SEAM DUE TO SWELLING.
- HYPOTHESIS -- INJECTION OF DRY CO_2 WILL DRY THE COAL, PARTICULARLY IN THOSE AREAS WHERE THE FLOW RATE IS HIGHEST.

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In any new area of science and technology it is often beneficial to formulate hypotheses and then work toward proving, disproving and refining them.

- HYPOTHESIS --BOTH LIQUID AND SUPERCRITICAL CO_2 MOVING THROUGH A COAL BED WILL EXTRACT SMALL MOLECULES TRAPPED WITHIN THE MACROMOLECULAR NETWORK. AS THE NETWORK RELAXES, THESE MOLECULES WILL BE RELEASED AND MOVE WITH THE FLOWING CO_2 AS LONG AS THE PRESSURE IS ABOVE THEIR THRESHOLD PRESSURE.

- HYPOTHESIS --SOME OF THE MINERALS COMMONLY FOUND IN COAL WILL DISSOLVE IN THE ACIDIC, CARBONATED WATER DURING THOSE TIMES WHEN BOTH WATER AND HIGH PRESSURE CO_2 ARE PRESENT TOGETHER IN THE COAL.

- HYPOTHESIS -- THERE WILL BE A PRESSURE, TEMPERATURE AND pH GRADIENT ACROSS THE COAL BED. WHEN DISSOLVED MINERALS AND ORGANICS REACH AREAS WITH LOWER PRESSURE, THEY WILL PRECIPITATE CAUSING THE PORES TO BEGIN TO CLOG.

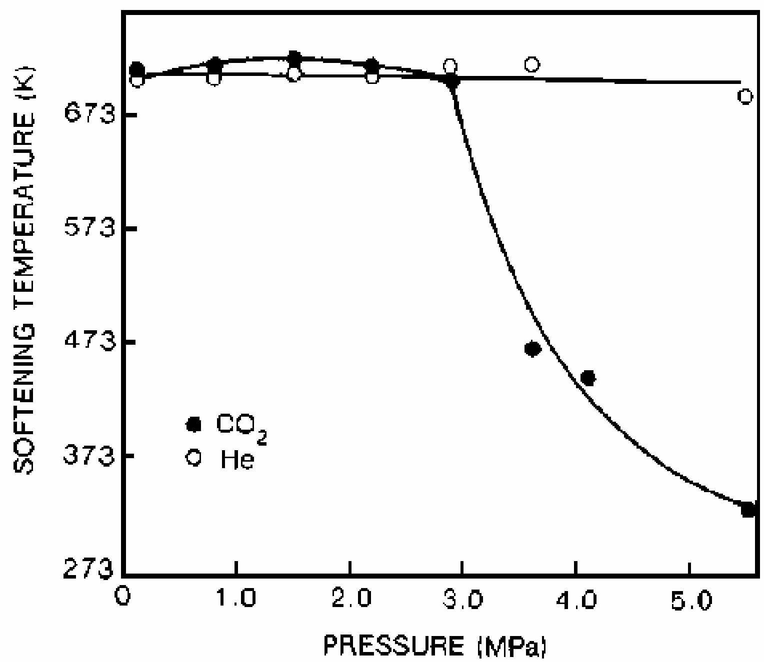
- HYPOTHESIS -- THE Ca AND Mg CONTENT OF THE COAL WILL DECREASE DUE TO DISSOLUTION OF CARBONATE MINERALS BY CARBONIC ACID AND DUE TO Ca AND Mg BEING DISPLACED FROM CARBOXYLIC ACIDS IN THE COAL.

EFFECT ON ORGANIC MATTER

Coal exists as either a glass or a rubber depending upon the temperature

GLASS
brittle
no large segmental molecular motion
diffusion of guest molecules is slow
diffusivity of guest molecules depends on size

RUBBER
flexible
macromolecule is free to move
diffusion of guest molecules is much faster
little size dependence upon diffusivity

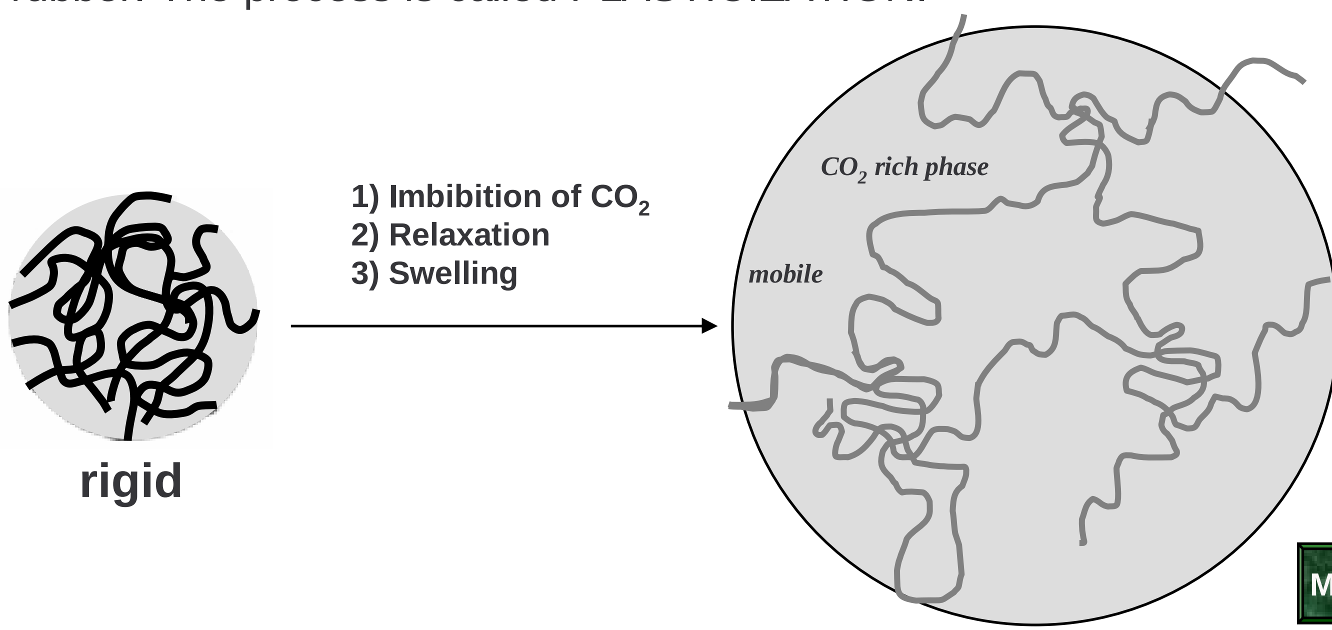


* Caveat, the coal in this experiment was free to swell.

M. R. Khan, R. G. Jenkins, *International Conference on Coal Science*, 1985, 903-906.

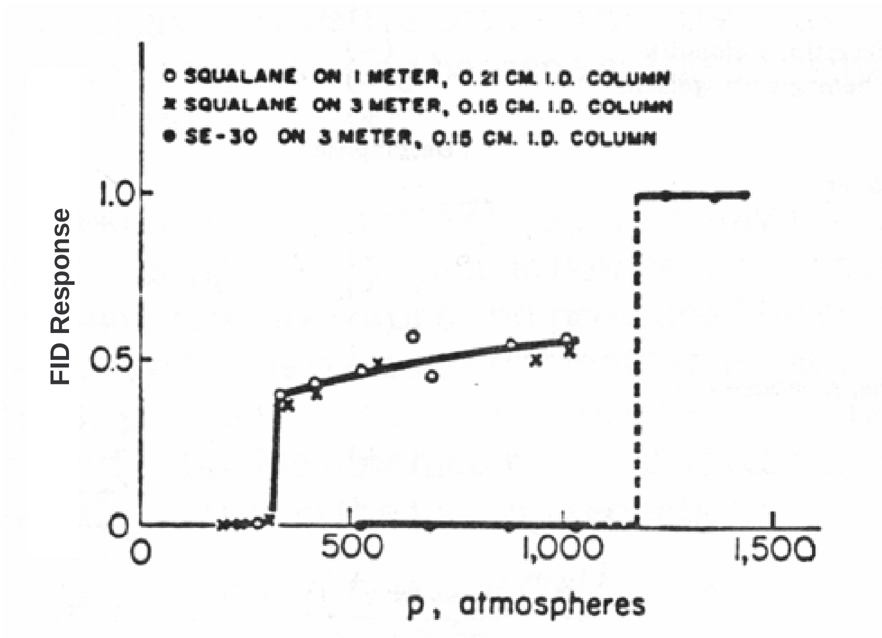
HYPOTHESIS--THE GLASS-TO-RUBBER TRANSITION TEMPERATURE (T_g) OF COAL WILL BE DRAMATICALLY REDUCED BY IMBIBITION OF CO_2. THE COAL WILL BECOME PLASTICIZED.

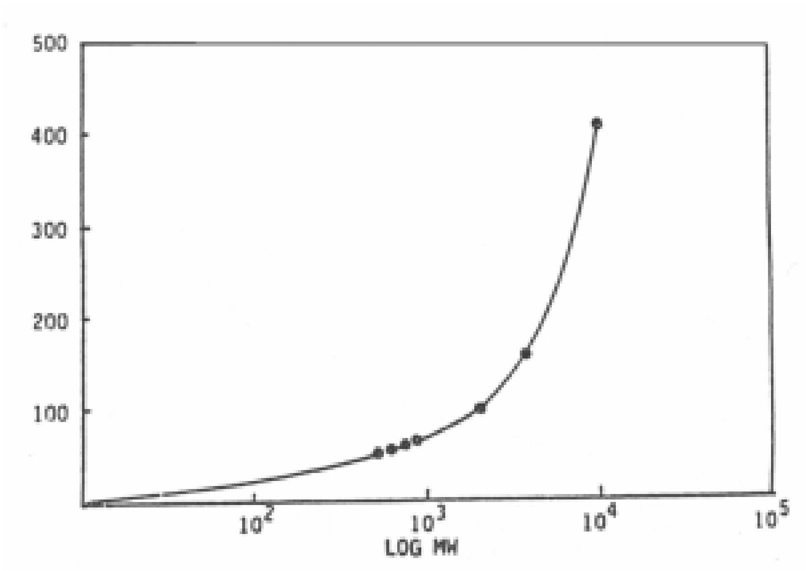
PLASTICIZATION
The temperature at which a coal is transformed from a glass to a rubber is known as the glass-to-rubber-transition temperature (T_g). When coals and other macromolecular systems such as polymers imbibe small molecules like CO_2 their glass-to-rubber-transition temperature can be decreased with pressure. The physical and chemical properties of coal change depending upon the state it is in, glass or rubber. The process is called PLASTICIZATION.



MOVIE

HYPOTHESIS --BOTH LIQUID AND SUPERCRITICAL CO_2 MOVING THROUGH A COAL BED WILL EXTRACT SMALL MOLECULES TRAPPED WITHIN THE MACROMOLECULAR NETWORK. AS THE NETWORK RELAXES, THESE MOLECULES WILL BE RELEASED AND MOVE WITH THE FLOWING CO_2 AS LONG AS THE PRESSURE IS ABOVE THEIR THRESHOLD PRESSURE.



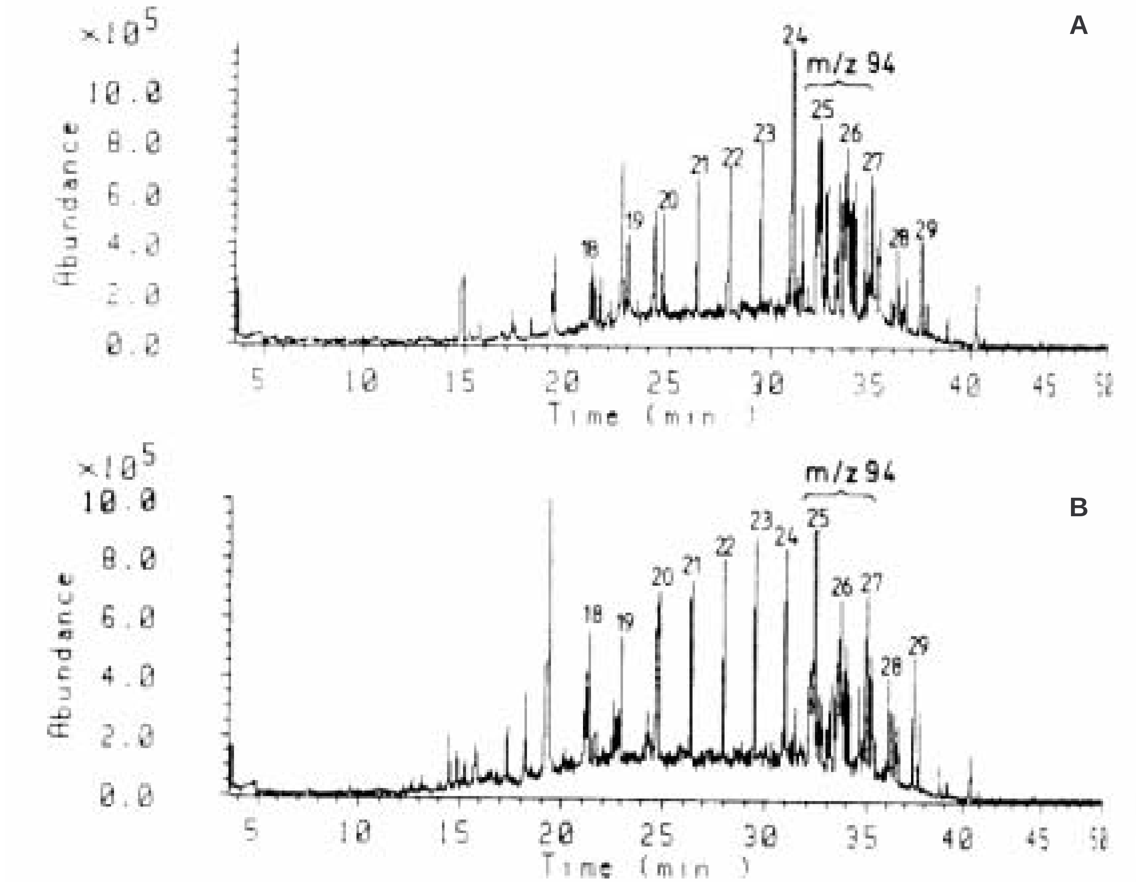


*Threshold pressure is that pressure where a solute just becomes soluble in moving, high-pressure CO_2. [1]

Among hydrocarbons the threshold pressure is an approximate function of their molecular weight.[2]

[1]J. C. Giddings, M. N. Myers, J. W. King, Dense-Gas Chromatography at Pressures up to 2000 Atmospheres, *J. Chromatographic Sci.* 1969, 7, 276-283.
[2]Lyle Bowman, Dense Gas Chromatographic Studies, Dissertation, University Of Utah, 1976.

HYPOTHESIS -- THERE WILL BE A PRESSURE, TEMPERATURE AND pH GRADIENT ACROSS THE COAL BED. WHEN DISSOLVED MINERALS AND ORGANICS REACH AREAS WITH LOWER PRESSURE, THEY WILL PRECIPITATE CAUSING THE PORES TO BEGIN TO CLOG.

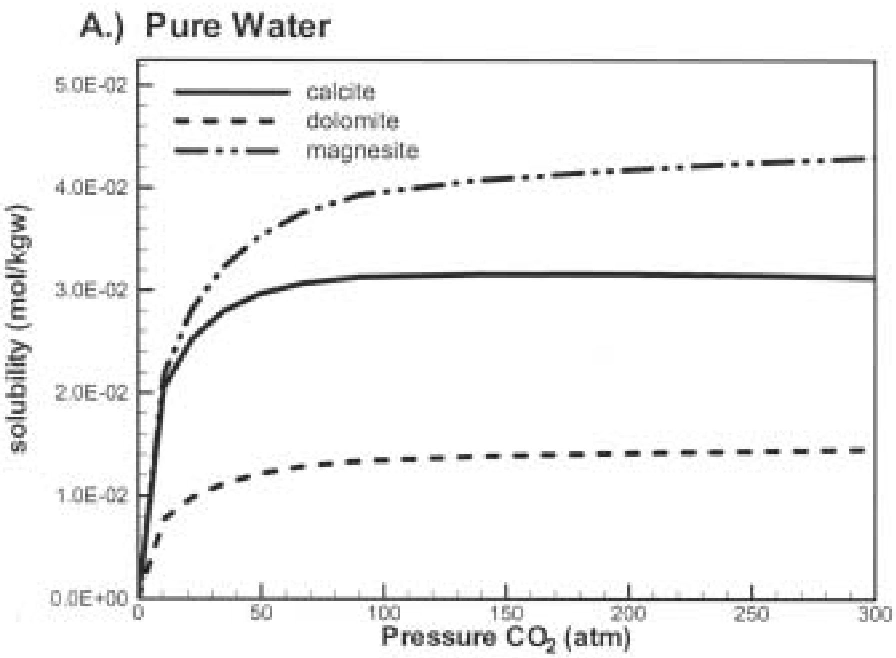


Total ion chromatograms of the carbon dioxide extracts from (A) a peat and (B) a low rank coal. Numbers correspond to chain lengths of *n*-alkanes.

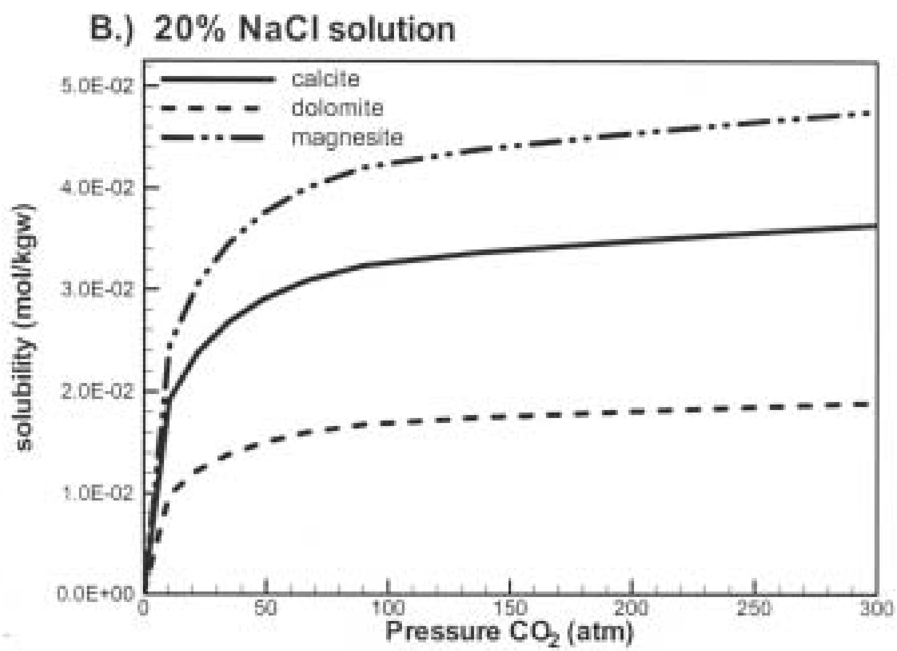
Taken from F. Martin, T. Verdejo and F. J. Gonzalez-Vila, *Journal of Chromatography*, 1992, 607, 377-379.

HYPOTHESIS--SOME OF THE MINERALS COMMONLY FOUND IN COAL WILL DISSOLVE IN THE ACIDIC, CARBONATED WATER DURING THOSE TIMES WHEN BOTH WATER AND HIGH PRESSURE CO_2 ARE PRESENT TOGETHER IN THE COAL.

SOLUBILITY OF VARIOUS MINERALS ASSOCIATED WITH COAL IN CARBONATED WATER AND BRINE AS A FUNCTION OF PRESSURE AT 50^{O}C.



Estimated using PHREEQC.



Estimated using Geochemist's Workbench.

HYPOTHESIS -- INJECTION OF DRY CO_2 WILL DRY THE COAL, PARTICULARLY IN THOSE AREAS WERE THE FLOW RATE IS HIGHEST.

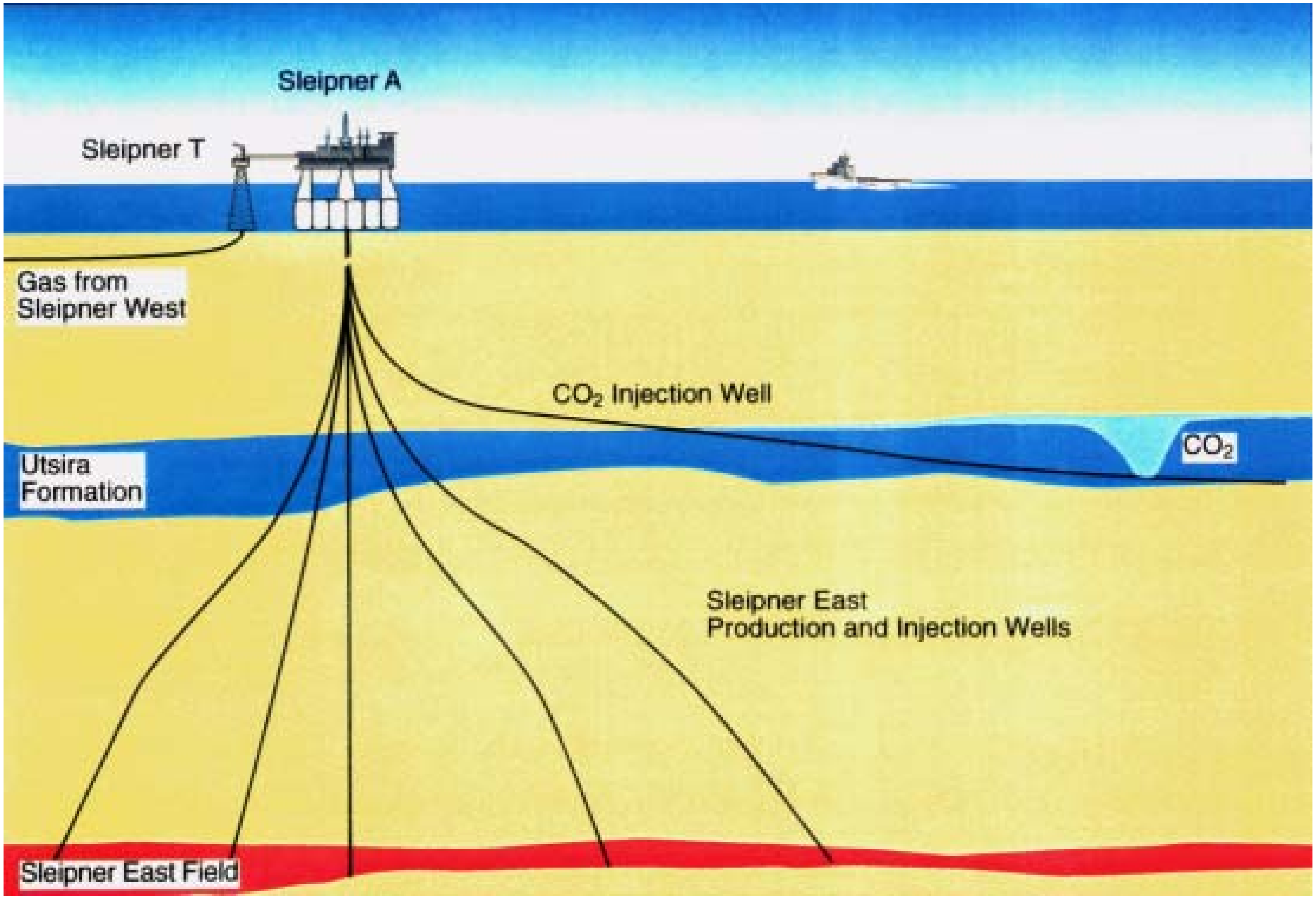
- Iwai *et al.*[1] report the use of supercritical CO_2 to dry coal. They showed that drying of ground and sieved coal (8 grams, 18-30 mesh) with CO_2 (1.5 moles/hour for 20 hours) at either 9.8 or 14.7 MPa and 40°C resulted in removal of water and increased both the surface area and the pore volume of the coal.
  - The degree of drying that occurs is unknown, but will probably not be quantitative except near the injection well.
  - Water could be removed by either becoming solubilized by CO_2 or by being displaced by CO_2. Under some conditions water is almost quantitatively removed from low rank coals.

Table 1
Water contents in coal samples

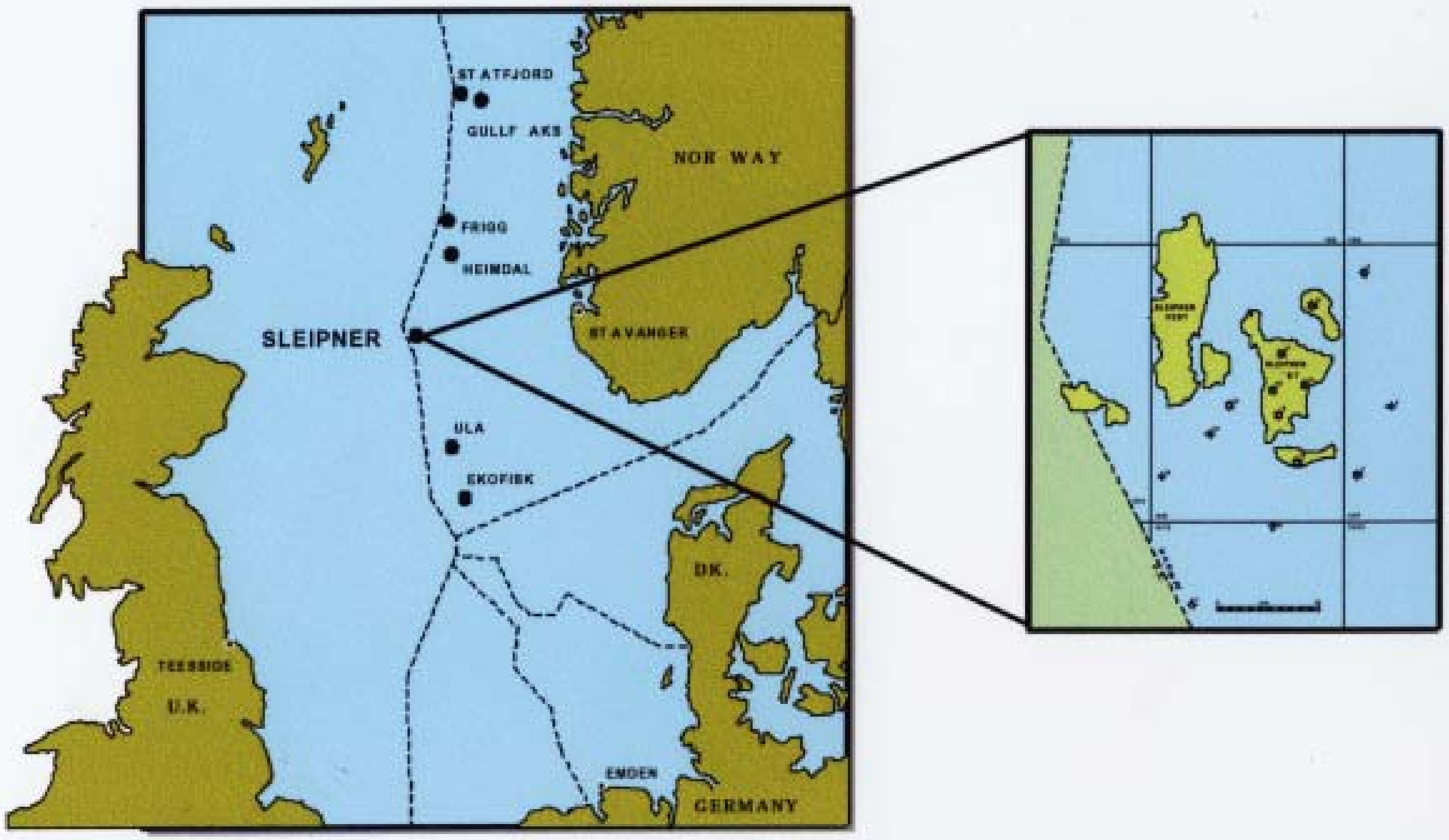
Sample	Berau coal (g-water/g-dried coal)	Taiheiyo coal (g-water/g-dried coal)
Supercritical drying (14.7 MPa)	0.0188	0.0100
Thermal drying (110°C)	0.0153	0.0091
Raw coal	0.2271	0.0622

1) Y. Iwai, T. Murozono, Y. Koujina, Y. Arai, K. Sakanishi, *J. Supercritical Fluid* 2000, 18, 73-79.

BRINEFIELD SEQUESTRATION
Sleipner Project



Sleipner Field Map



Sleipner Platforms

FIELD PILOTS PLANNED IN THE U.S.

FRIO FORMATION – TEXAS BUREAU OF ECONOMIC GEOLOGY

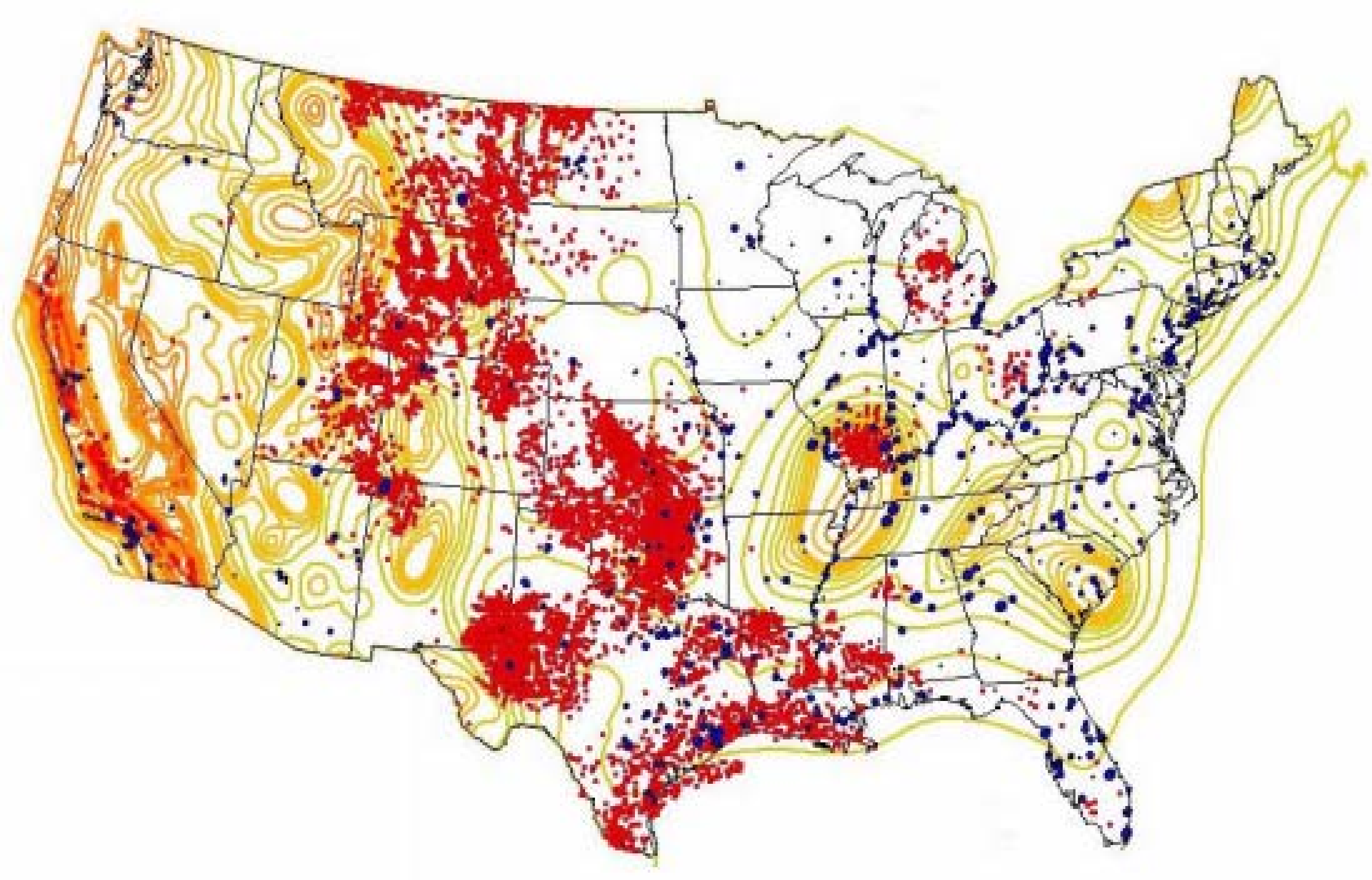
MOUNTAINEER PROJECT – NEW HAVEN, WV – MT. SIMON SANDSTONE SALINE FORMATION. AEP AND BATTELLE ARE STUDYING THE POSSIBILITY OF INJECTING CO_2 CAPTURED FROM THE 1300 MW MOUNTAINEER POWER PLANT.

Drilling Bits at Mountaineer Site (May 14, 2003)

Rig Setup at Mountaineer (May 19, 2003)

Mountaineer – Installation of 13-inch Casing

POWER PLANT LOCATIONS
BRINE WELL LOCATIONS
SEISMIC POTENTIAL



What happens when CO_2 is injected into a deep saline aquifer?

- Three processes describe the ultimate fate of the CO_2.
  1. Hydrodynamic trapping – keeps CO_2 as an undissolved gas that is trapped by an overlying low permeability caprock. Storage capacity is much greater at depths > 800m because CO_2 has a much greater density at those pressures.
  2. Solubility trapping – CO_2 is dissolved in the formation water

     Because CO_2 dissolution leads to lowering of the pH, it may initiate other chemical reactions. Most minerals are more soluble in acidic solutions, which can result in a buffering effect that consumes the H^+.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \quad (1)$$

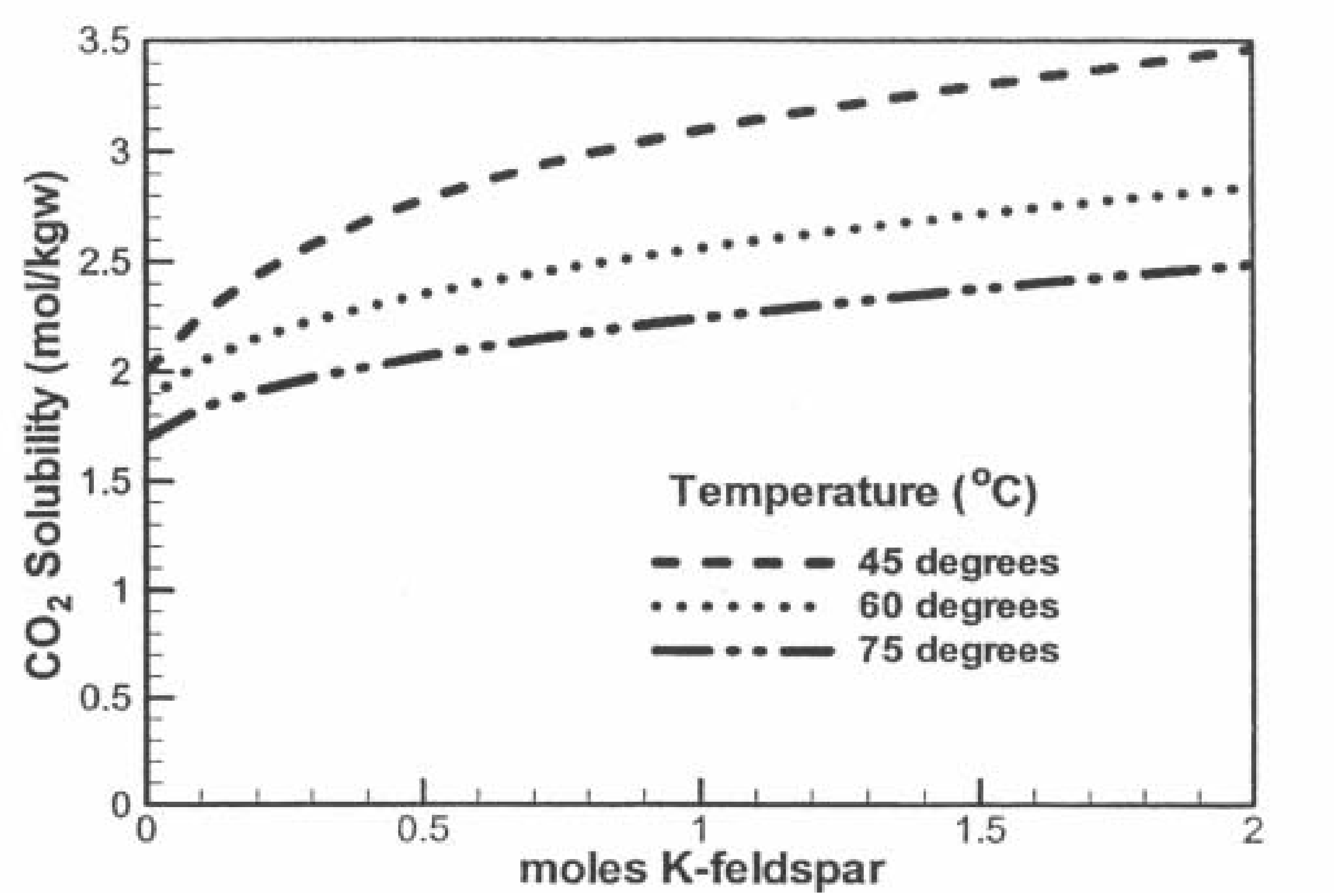
  3. Mineral trapping – dissolved CO_2 reacts with either aqueous species or the mineral matrix to precipitate as a solid such as $CaCO_3$, $MgCO_3$ or $FeCO_3$. This results in permanent storage and is not subject to leakage.

$$Ca^{++} + Mg^{++} + Fe^{++} + HCO_3^- \rightleftharpoons CaCO_3 + MgCO_3 + FeCO_3 + H^+$$

$$KAlSi_3O_8 + 4H^+ \rightleftharpoons K^+ + Al^{+3} + 3\ SiO_2 + 2H_2O\ (2)$$

K- feldspar

Consumption of H^+ enhances the forward direction of reaction (1) and increases the dissolution of CO_2



ENVIRONMENTAL, HEALTH, AND SAFETY CONCERNS

Seismic Activity Caused By Injection of Fluids Underground

Case study, Rocky Mountain Arsenal, 1960's

Existing regulations governing Deep Well injection

Environmental Aspects Of Geological Sequestration

Health effects of CO_2 – asphyxiant

Brine displacement into overlying aquifers

Hydrodynamic flow

Mobilization of trace metals

Produced water

Monitoring And Verification

Required for a 1000 years or more

Quantification of the amount of CO_2 sequestrated

Monitoring of it's long term integrity reduces risks

Simultaneous application of a wide variety of technologies

1. Tracers
2. CO_2 flux rates
3. Geophysical methods
4. All combined and integrated with reservoir simulation

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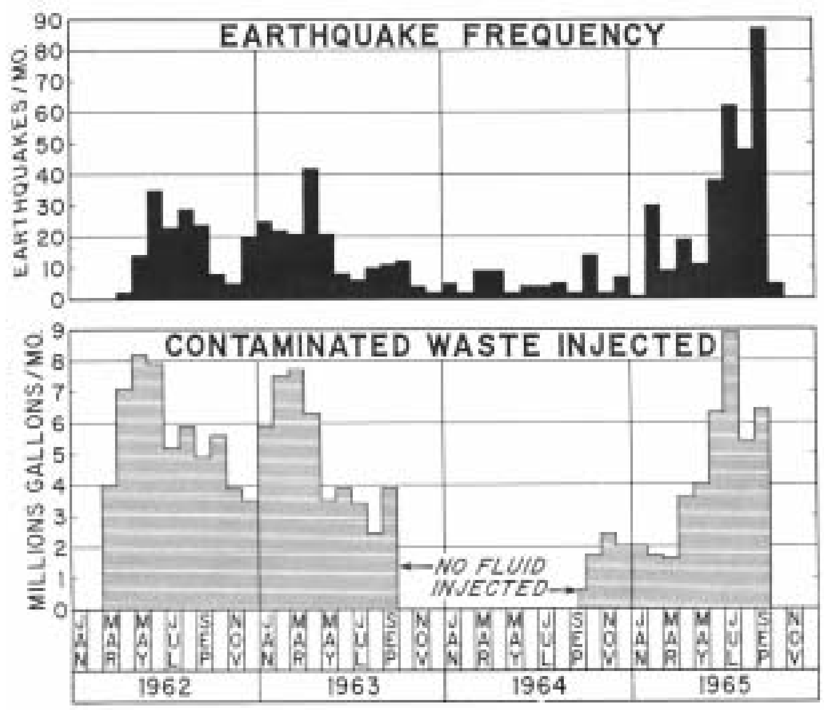
Anthropogenic Seismic Activity

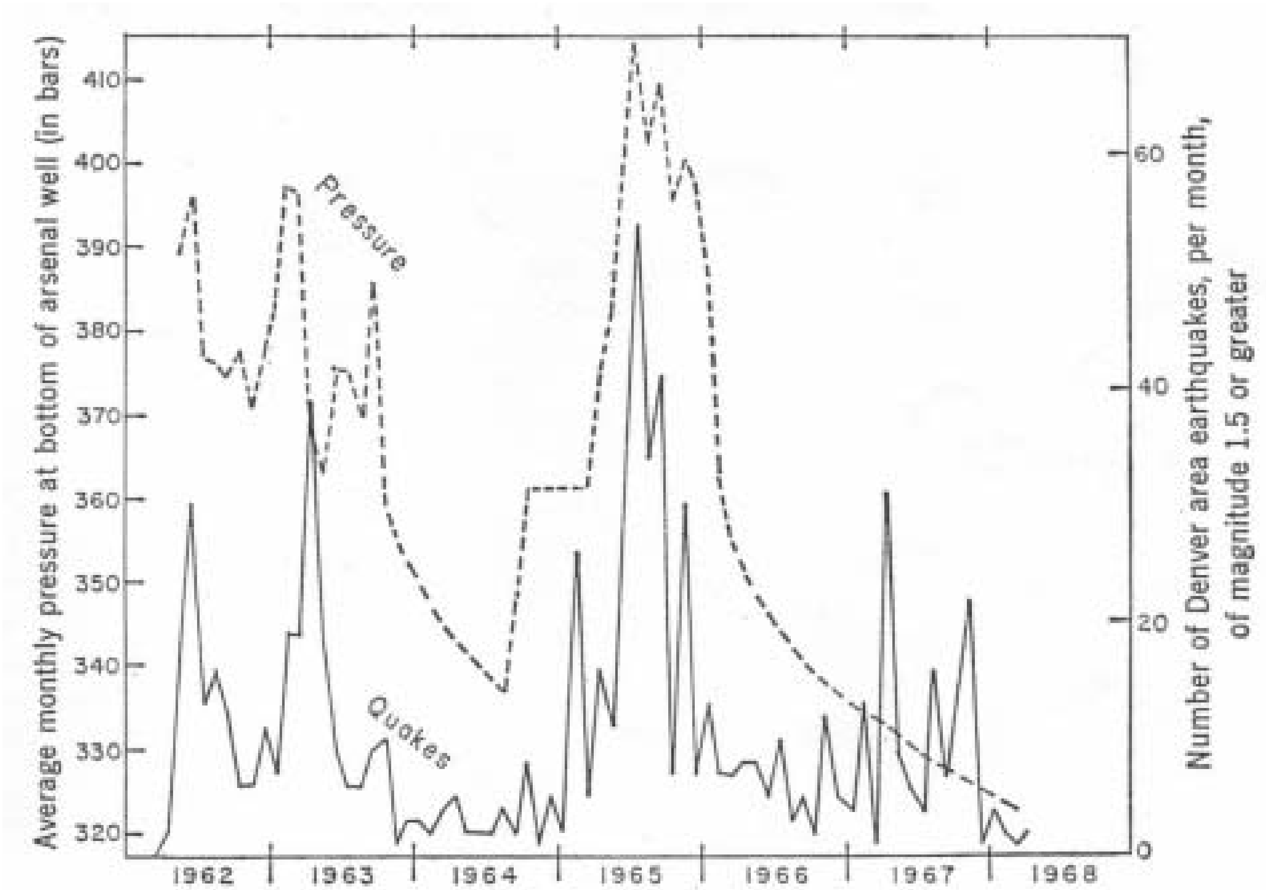
1. **There are dozens of well documented cases of anthropogenic earthquakes**
2. **The Denver earthquakes[1]**
   - Starting in April 1962, more than 700 earthquakes
   - Magnitude small, but April 1967 there was a 5 Richter scale quake
   - No previously recorded seismic activity
   - In 1966 D.M. Evans suggested a direct relationship between seismic activity and waste water injection from chemical mfg at the Rocky Mountain Arsenal
   - 3.7 km disposal well
   - Quakes started one month after injection began
   - Direct relationship between quake frequency and volume of fluid injected



1. Evans, D.M., Man-Made Earthquakes In Denver, *Geotimes* **1966**, 10, 11-17.

Anthropogenic Seismic Activity

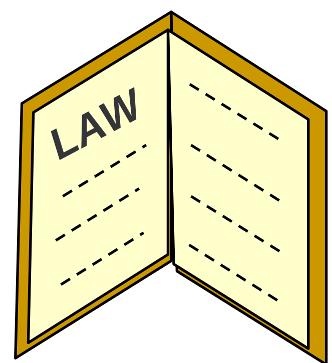
Relationship between well head pressure and seismic activity. The increase in seismic activity in 1967 when average pressure was decreasing shows that it isn't a simple relationship.[1]



1. Healy, J. H.; Rubey, W.W.; Griggs, D. T.; Raleigh, C. B., The Denver Earthquakes, *Science* **1968**, 161, 1301-1310.

EXISTING REGULATIONS GOVERNING DEEP WELL INJECTION

- Underground Injection Control (UIC) program
  - Regulates all underground fluid disposal
  - Defines 5 classes of injection wells
  - Injection into a deep saline aquifer falls under class I, defined as “Injection beneath the lowermost formation with potential to be a USDW.”
    - Deepest and most strictly regulated
    - Injection of hazardous materials is permitted
    - Must have a thick, impermeable caprock
    - Must not be seismically active
    - Strict construction regulations
    - Strict monitoring requirements – 24 h/d



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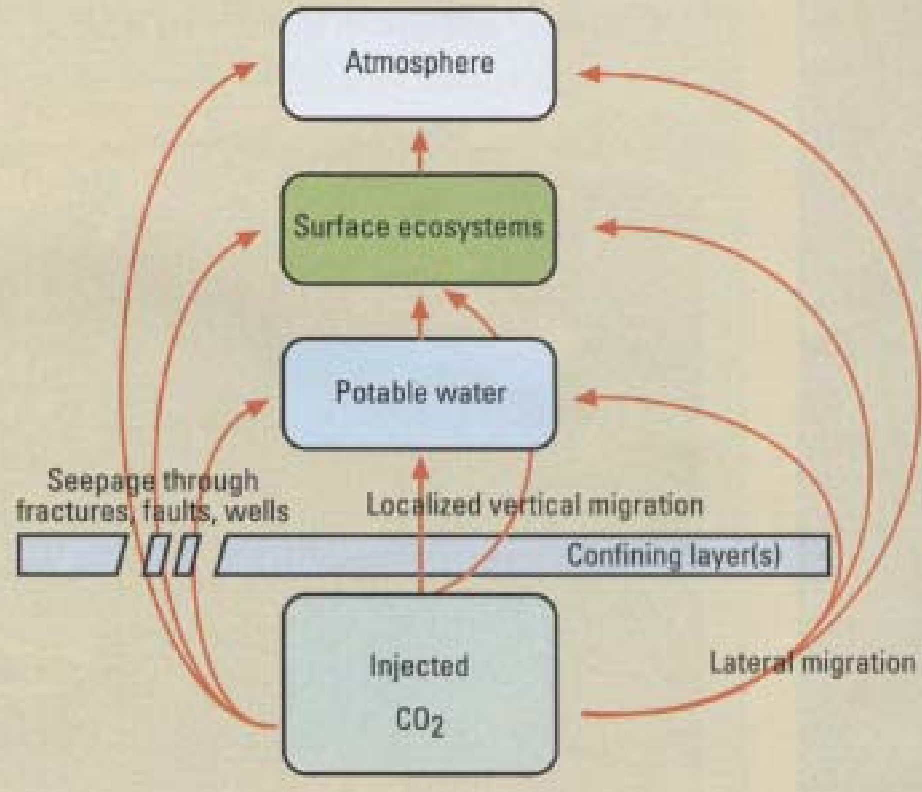
Typical Monitoring Requirements for a Class I Underground Injection Facility.[390]

Parameter	Monitoring Requirements	Reporting Requirements
Injection Pressure	Continuous	Monthly
Bottomhole Pressure		Monthly
Annulus Pressure	Continuous	Monthly
Interannulus Pressure	Continuous	Monthly
Temperature	Continuous	Monthly
Flowrate	Continuous	Monthly
Specific Gravity	Weekly	Monthly
pH	Weekly	Monthly
Composition of Injectate	Every 6 months	Monthly
Cumulative Volume	Daily	Monthly
Annulus Sight Glass Level	Daily	Monthly
Groundwater monitoring	Quarterly	Quarterly
Seismic monitoring (if required)	Continuous	Monthly

Sminchak, J.; Gupta, N.; Byrer, C.; Bergman, P., Issues Related To Seismic Activity Induced By Injection of CO_2 In Deep Saline Aquifers, First National Conference on Carbon Sequestration, available at www.netl.doe.gov.

Potential pathways for CO_2 leakage from deep saline aquifers

Localized vertical migration may be driven by large pressure gradients near the injection well. Lateral migration occurs as CO_2 moves around the edges of the confining layers. Significant seepage may occur through natural and induced fractures and faults in the confining layers and through existing wells.



Bruant, R. G.; Guswa, A. J.; Celia, M. A.; Peters, C. A., Safe storage of CO_2 in Saline Aquifers, *Environ. Sci. Technol*. **2002**, 36, 240A -245A.

ENVIRONMENTAL ASPECTS OF GEOLOGICAL SEQUESTRATION

1. **CO_2 is an asphyxiant -10% CO_2 causes unconsciousness and death**
2. **OSHA Standard – 5000 ppm 8 h TWA**
3. **Brine displacement into an overlying fresh water aquifer**
4. **Hydrodynamic flow through a coalbed could carry away sequestered CO_2 over geological time**
5. **If leaking CO_2 reaches shallow drinking water it could mobilize trace metals**
6. **Increased CH_4 surface flux associated with CO_2– ECBM**

Composition of CBM produced waters

Some water compositions for produced water from coalbed methane and conventional natural gas extraction in the USA.[403]

Parameter	Coalbed methane	Natural gas
pH	7.8	7
Major components, mg/1		
Total dissolved solids (TDS)	4000	20000-100000
Total suspended solids (TSS)		1.0
Chloride (Cl^-)	2000	11000
Sulphate (SO_4^{2-})	12.9	0-400
Bicarbonate (HCO_3^-)	597	
Carbonate (CO_3^{2-})	0.008	
Fluoride (F^-)	2.6	
Nitrate (NO_3^-)	3.0	
Fe	10	
Ca	89	
Na	1906	
K	7.5	

Sloss, L. L.; Davidson, R. M.; Clarke, L. B., *Coalbed Methane Extraction*, IEA London, **1995**

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Composition of CBM produced waters

Trace elements and hydrocarbons, μg/l		
Ag	1.1	10-70
Al	40	
As		30
Ba	2780	10-100
Cd	5	30
Cr	3	20-230
Cu	5.6	0-100
Hg	0.13	1
Li	92	
Mn	250	
Ni	29	100
Pb	55	100-170
Sb	30	70
Se	25	60
Sr	4000	
Tl		90
V	5	
Zn	109	40-200

Sloss, L. L.; Davidson, R. M.; Clarke, L. B., *Coalbed Methane Extraction*, IEA London, **1995**

MONTIORING AND VERIFICATION

1. **Maybe required for more than 1000 yrs – Quantification of the amount of CO_2 and validating that it remains in the formation requires simultaneous application of a wide variety of techniques**
   - **Tracers**
   - **CO_2 + CH_4 soil gas flux**
   - **Geophysical methods**
   - **Combined and integrated with reservoir simulation**
2. **Rate of migration of CO_2 and CH_4 to the surface is needed**
3. **Has the potential to prevent catastrophes, protect public health and safety, and reduce risks**

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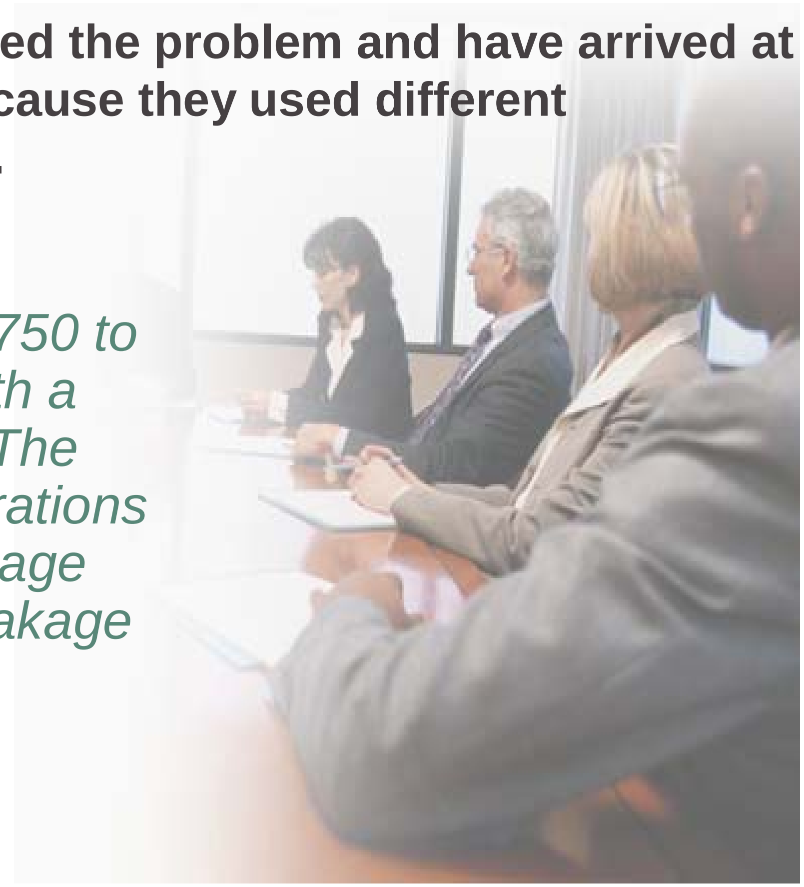
HOW MUCH LEAKAGE IS ACCEPTABLE?

The second law of thermodynamics demands that all of the CO_2 will not reside permanently in the sequestration formation. Entropy is working against us. It will leak.

Multiple research groups have addressed the problem and have arrived at very different answers, in large part because they used different assumptions and different approaches.

"In some cases, the reduction from 750 to 450 ppm would be possible even with a mean (leak) rate of 1%/yr or more. The results imply that economic considerations are likely to constrain allowable leakage rates more tightly than impacts of leakage on global atmospheric CO_2."[1]



1. Pacala, S. W., Global Constraints on Reservoir Leakage,*Proceedings GHGT-6* Kyoto, Japan **2002**, B2-4.

HOW MUCH LEAKAGE IS ACCEPTABLE?

Hepple and Benson also addressed the question. "*With few exceptions, seepage rates of 1%/yr were unacceptably high. For stabilization at 350, 450 and 500 ppmv, seepage rates must be less than 0.01%/yr to be acceptable for all scenarios*."[1]

Dooley and Wise evaluated the consequences of leakage rates of 1% and 0.1%/yr. "*With a hypothetical leakage rate of 0.1%/yr after 2035, the incremental impact on required net annual carbon emissions reductions does not appear substantial. However, a 1%/yr leakage rate would have an enormous impact on emission targets. With a 1%/yr leakage rate, net annual carbon emissions would have to be negative by last half of the century*."[2]

[1]Hepple, R. P.; Benson, S. M., Implications of surface seepage on the effectiveness of geologic storage of carbon dioxide as a climate change mitigation strategy, in *Proceedings GHGT-6*, Kyoto, Japan, **2002**, A2-3.

[2]Dooley, J. J.; Wise, M. A., Why injecting CO_2 into various geologic formations is not the same as climate change mitigation:The issue of leakage, in *Proceedings GHGT-6*, Kyoto, Japan, **2002**, B2-5.

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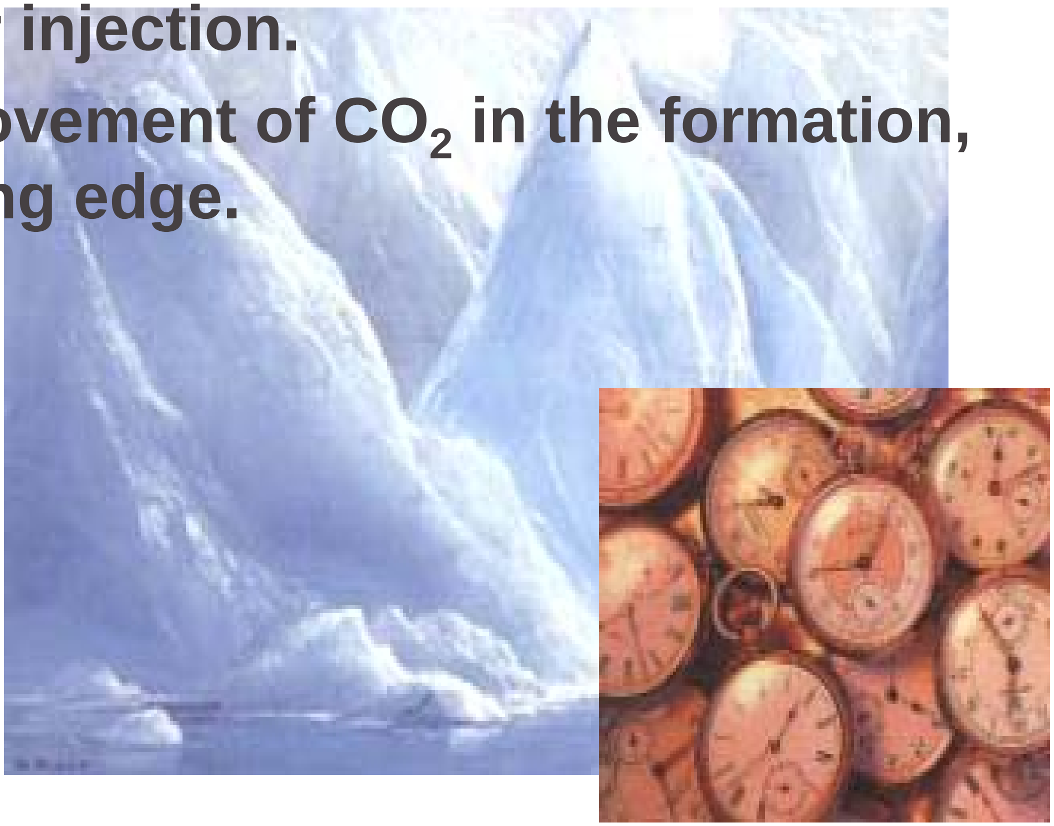
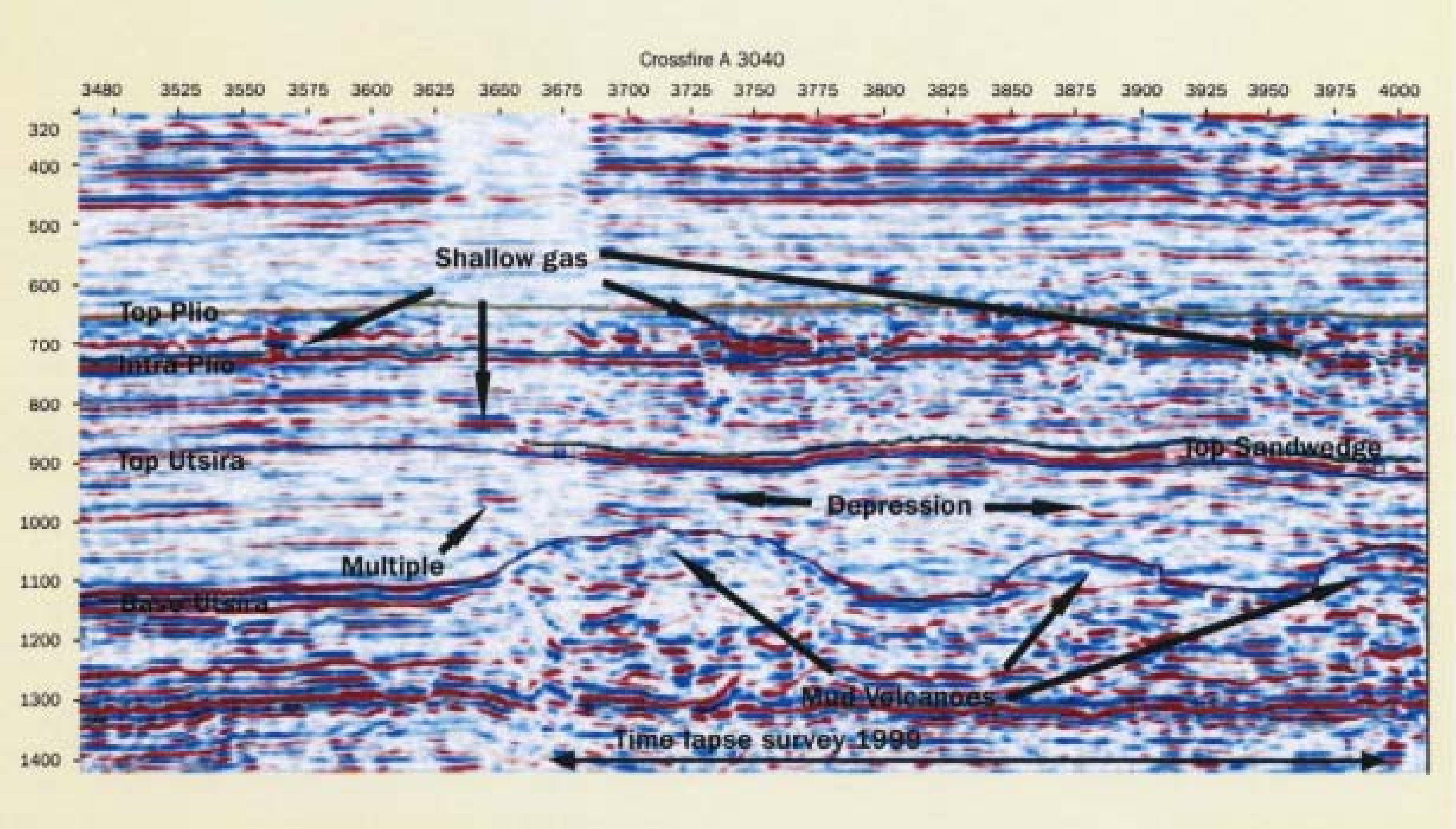
GEOPHYSICAL MONITORING RESULTS FROM SLEIPNER – 4D SEISMIC

1. Allows the observation of moving CO_2 in the reservoir. Careful 3D Seismic Surveys before, during and after injection.
2. Used to map movement of CO_2 in the formation, locate the leading edge.

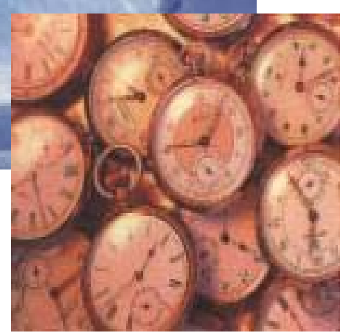


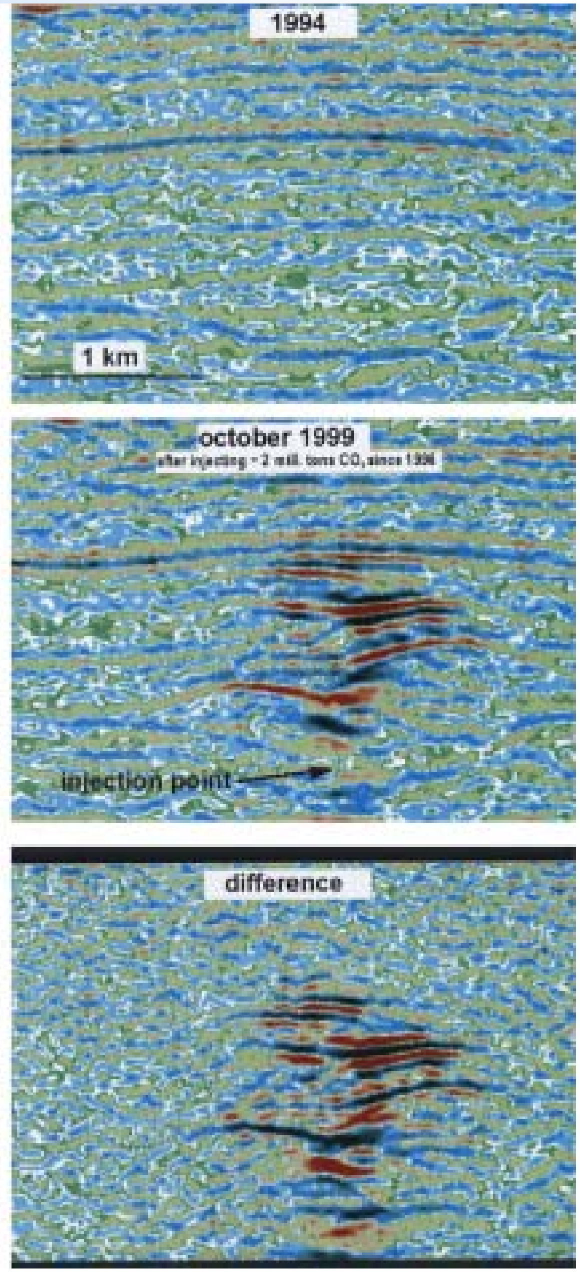
Preinjection seismic survey results from Sleipner. Reveals the presence of (*1*) mounds of mud at the base of the Utsira sandstone formation, (*2*) up to 14 thin shale layers interspersed in the sandstone, and (*3*) a thick Pilocene caprock divided into two units.



Arts, R.; Brevik, I.; Eiken, O.; Solle, R.; Causse, E.; van der Meer, B., *Geophysical Methods for Monitoring Marine Aquifer CO_2 Storage – Sleipner Experiences*. *GHGT-5*, Cairns, Australia, **2000.**

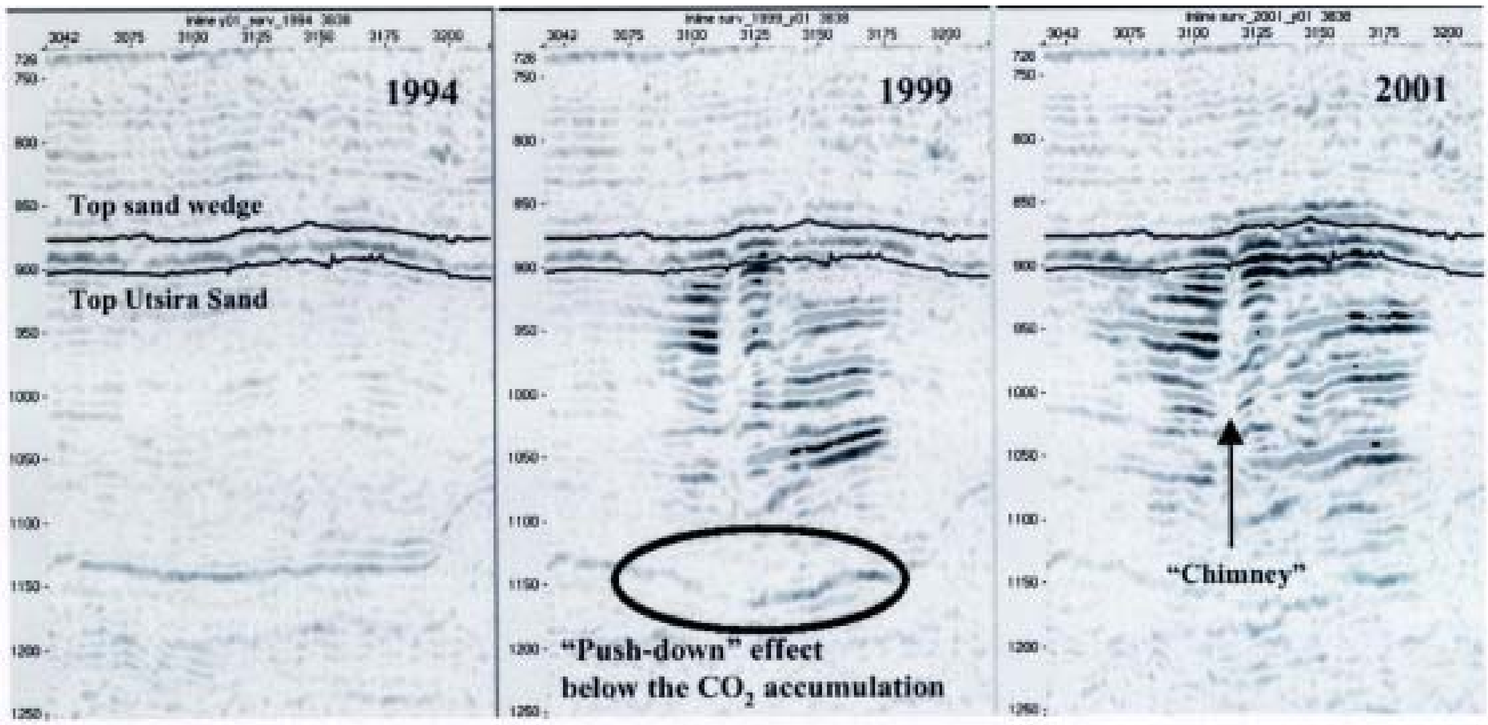
Time lapsed results from the seismic surveys at Sleipner. The presence of lateral lines indicate ponding of CO_2 under intrareservoir shale layers that act as barriers to flow.





Results from the 1994, 1999 (after 2.5 Mt of CO2 Injected) and 2001 Seismic Surveys at Sleipner.

There is good consistency between the 1999 and 2001 results. Gas at various levels in the formation is trapped under the thin shale layers. By 1999 only a small amount of CO_2 reached the caprock where it is confined. The 2001 results show a larger lateral distribution of CO_2. The two reflections at the top of the Utsira formation in the 2001 survey represent accumulation of CO_2 at the caprock. The pronounced "chimney" is located above the injection well and shows vertical migration of CO_2.



Arts, R.; Eiken, O.; Chadwick, A.; Zweigel, P. M. L., B.; Monitoring CO_2 Injected At Sleipner Using Time Lapsed Seismic Data, *Proceedings GHGT-6*, Kyoto, Japan, **2002**.

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CONCLUSIONS

1. By 2012 the gap between "Business as Anticipated" and the target will be 0.39 Gt CO_2.
2. The 18% Reduction in GHG intensity can not be met without including contributions from geological sequestration.
3. Capture of CO_2 from large fossil fuel fired electric power generating stations and gasification facilities is being done today with off-the-shelf technologies; however, the economics are not favorable.
4. CO_2 has already been successfully stored in both coal seams and deep saline aquifers on a commercial scale using off-the-shelf technologies.
5. There is more than 30 years of commercial application experience for CO_2 injection into depleted petroleum reserves for EOR purposes.
6. The above combine to make a compelling argument that sequestration in geological formations represents a safe, practical and viable approach to meeting the President's GCCI Target.


CO_2
CH_4