CO_2 Sequestration in Spent Oil Shale Retorts

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CO_2 emissions from oil shale processing must be addressed

- Burnham and McConaghy, LLNL, 26th Oil Shale Symposium

- A mitigation cost of ~$30/ton CO_2 will shift economics to lower carbonate decomposition and easier CO_2 sequestration*
  - HRS: 0.13 tons/bbl = $4/bbl, not counting CO_2 emissions from excess carbon combustion used to generate electricity
  - MIS: 0.46 tons/bbl = $14/bbl
  - ICP: 0.06-0.16 tons/bbl = $2-5/bbl, depending on direct or electrical heating and the efficiency of the electricity generation

  **burning shale oil makes 0.45 tons/bbl*

- Friedmann, LLNL, 26th Oil Shale Symposium

  "The US oil shale industry will be delayed or impeded if it is not proactive with regard to carbon management"

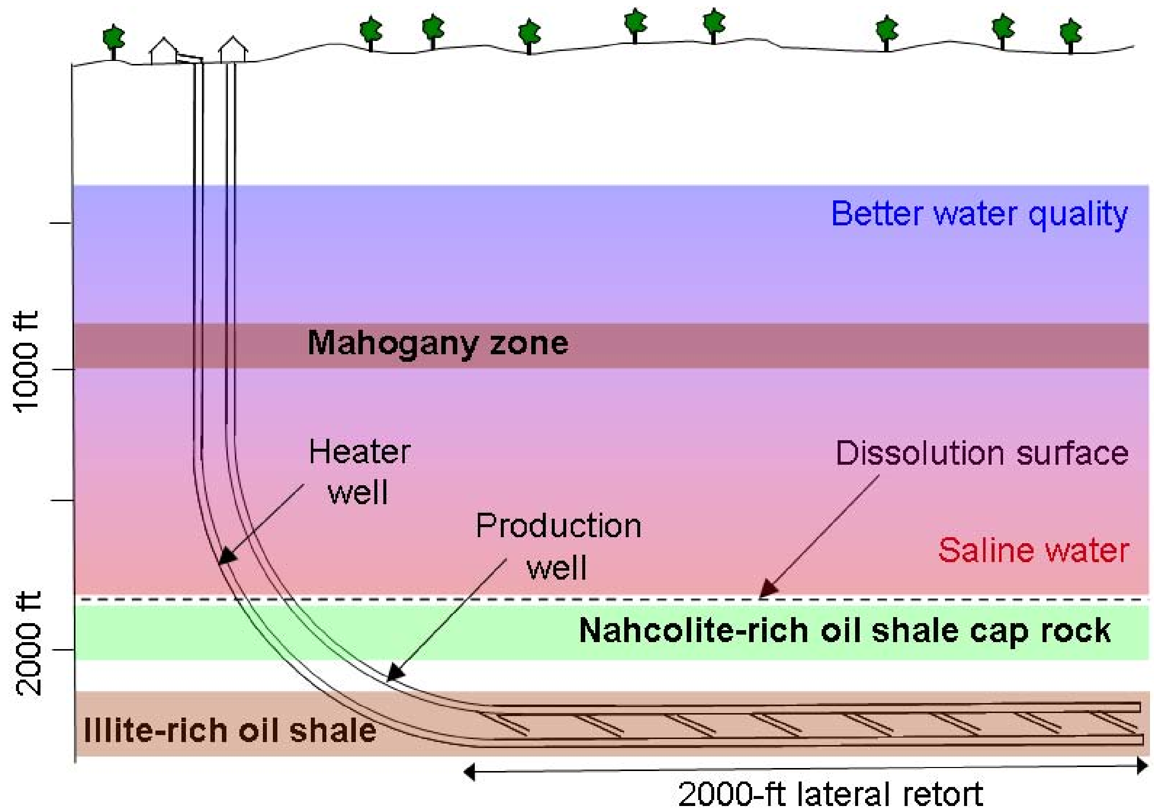
Brandt did a more detailed analysis of ATP (ex-situ) and ICP (in-situ) emissions

A. Brandt, 27th Oil Shale Symposium		Heat required, MJ/MJ of FFD		CO_2 emitted, gCeq/MJ of FFD	
		ICP	ATP	ICP	ATP
High Case	Production	0.59	0.37	13.5	17.5
	Refining	0.12	0.16	2.5	3.5
	Total	**0.71**	**0.53**	**16**	**21**
Low Case	Production	0.34	0.27	5.5	14
	Refining	0.11	0.14	2	3.4
	Total	**0.45**	**0.41**	**7.5**	**17.4**

- Use of the Final Fuel Delivered (FFD) generates another 20 gCeq/MJ of FFD
- Conventional petroleum generates a total of 25 gCeq/MJ of FFD

The baseline AMSO concept now uses a horizontal, sealed downhole burner

- Counter-current heat exchange maximizes thermal efficiency
- Various burner designs with enriched O_2 and recycled CO_2 are being evaluated

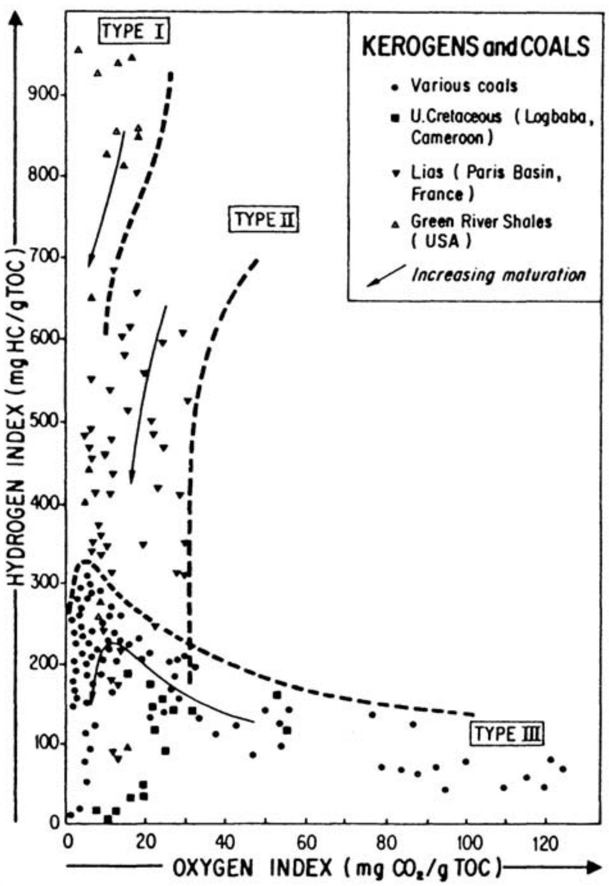


CO_2 emissions can be reduced by improving thermal efficiency

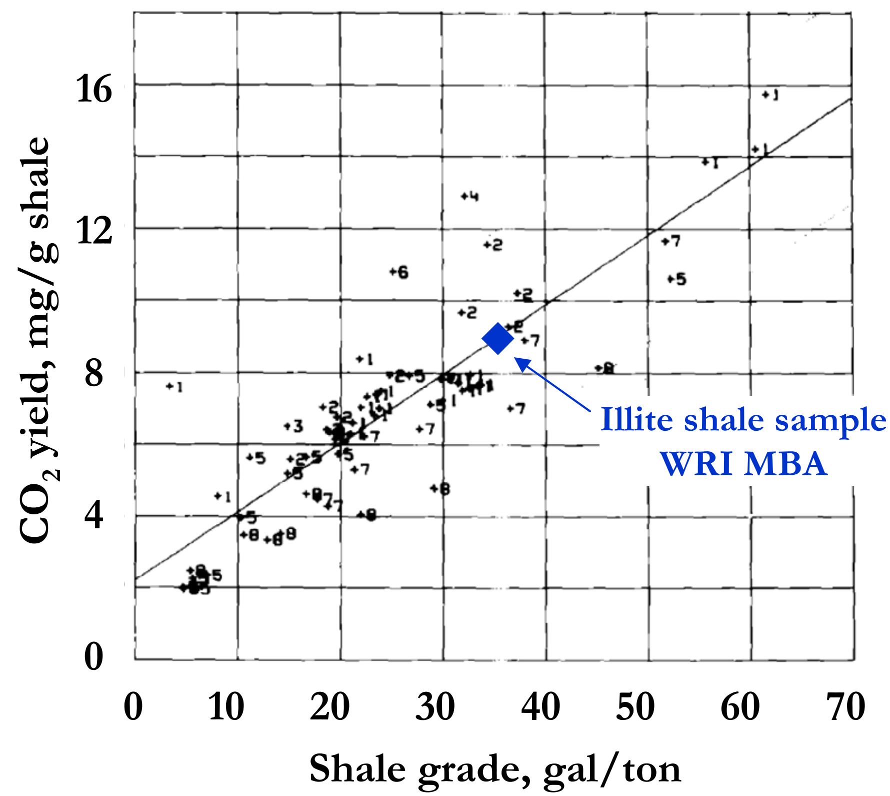
- Energy needed/barrel depends on water content and process efficiencies
  - In-situ processing of 27 gal/ton shale takes ~1 GJ/bbl, assuming 5 wt% water and 75% Fischer Assay recovered yield by volume
  - Recovered shale oil has an energy content of 6 GJ/bbl (6:1 gain)
    - For comparison, electricity with 50% conversion efficiency gives 3:1 gain
- CO_2 generated/barrel depends on how the heat is delivered
  - Natural gas gives 55 kg CO_2/GJ thermal = 55 kg/in-situ bbl
  - Pyrolysis generates 15 kg CO_2/in-situ bbl
  - Assuming heat losses and heat recapture cancel
    - 70 kg CO_2/in-situ bbl= 3.2 gCeq/MJ shale oil
  - With refining and transportation losses, ~6 gCeq/MJ final fuel
    - For comparison, Brandt gives 8-17 gCeq/MJ final fuel for Shell ICP
    - Brandt also gives ~5 gCeq/MJ final fuel for conventional petroleum

Illite shale gives a comparable amount of CO_2 from pyrolysis as typical marlstone

CO_2 yields depend on mineralogy, kerogen type, and maturity



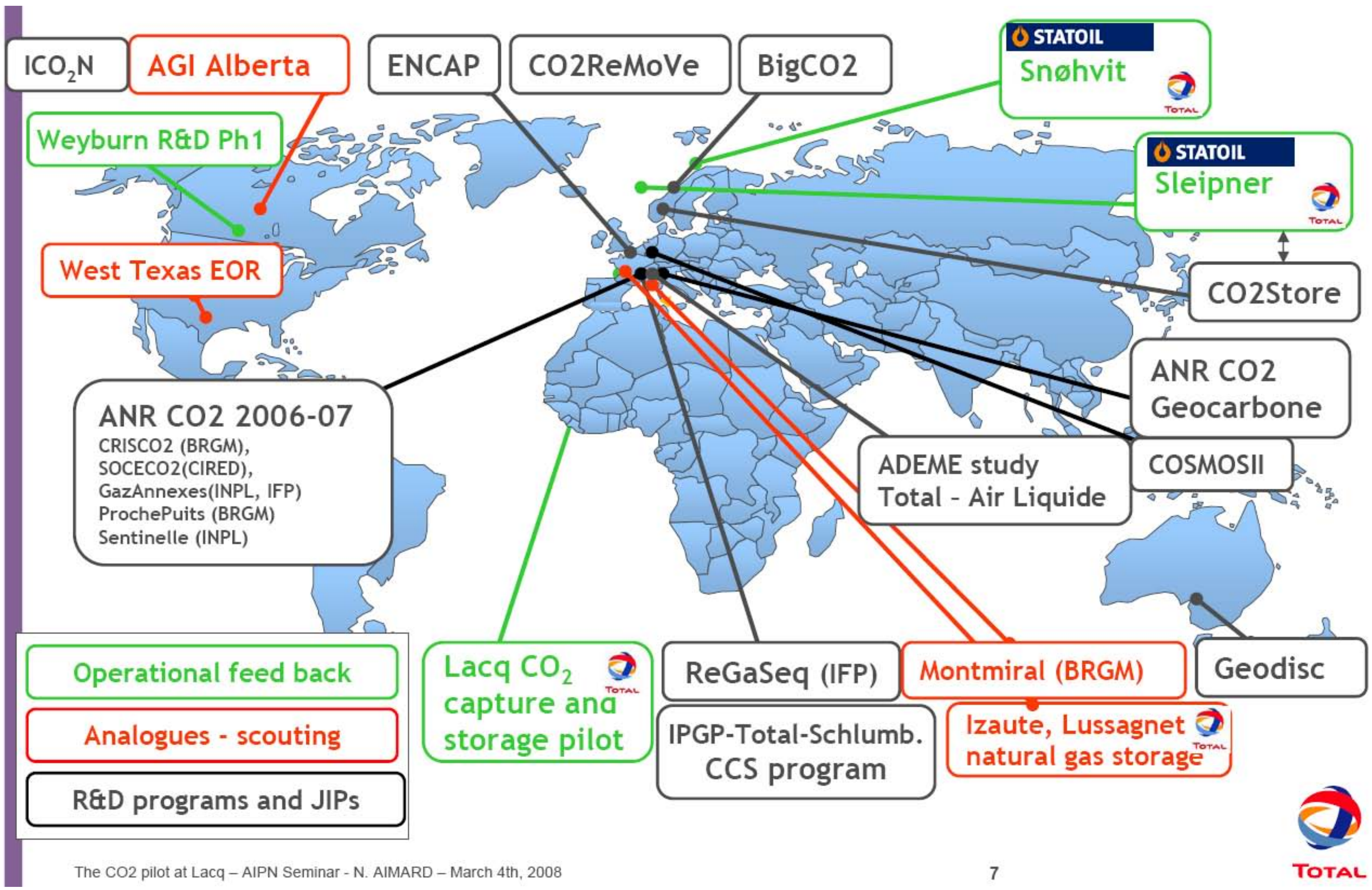
From Singleton et al. (1986) LLNL Material Balanced Assay



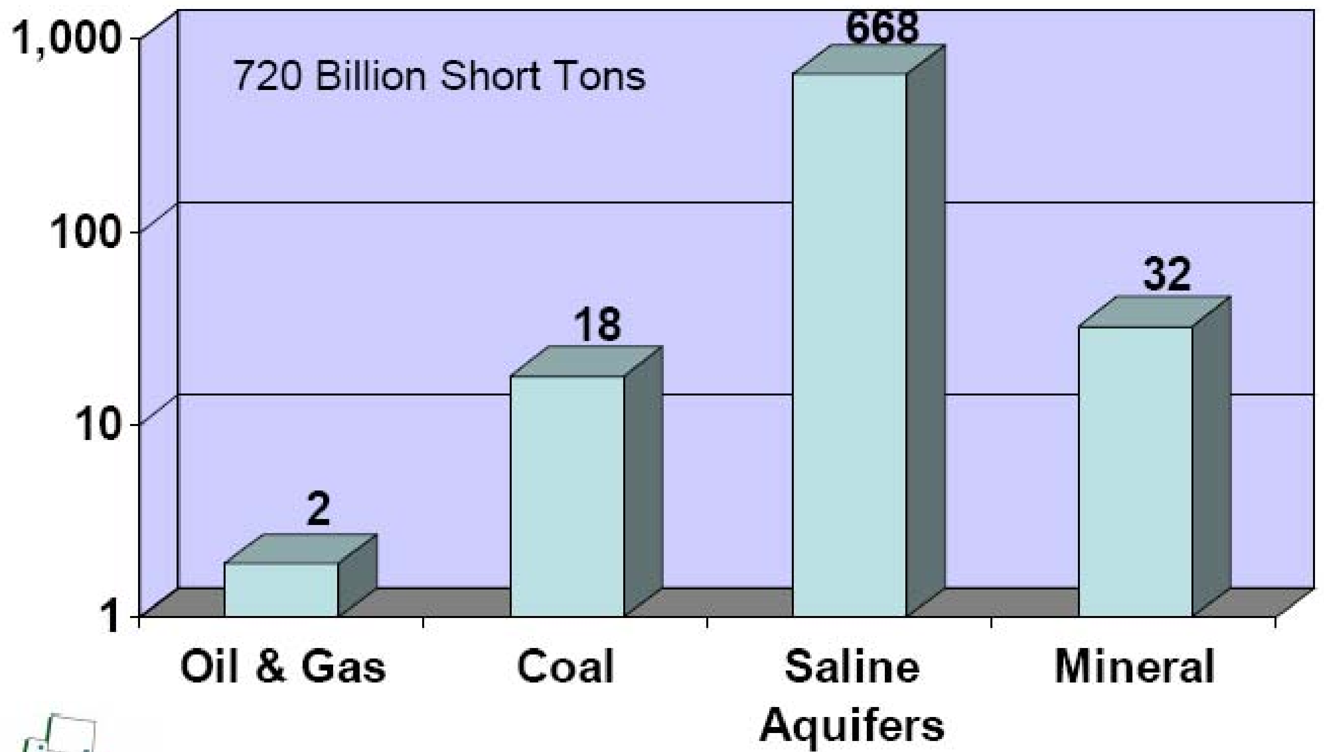
CO_2 emissions can be minimized by sequestering produced CO_2

- Three possible ways of reducing CO_2 should be evaluated
  - Disposal in deep geologic formations
  - Sale for enhanced oil recovery
  - Mineralization in spent retorts
- Spent retorts might be able to store all the CO_2
  - There is enough porosity
  - There are brines available in the area from natural gas wells and on-site aquifers—one might concentrate them with distillation or ROM
  - High residual temperatures will enhance mineralization kinetics

There are a variety of large-scale CO_2 sequestration experiments in the world



The Colorado Geological Survey has estimated carbon storage potential in Colorado



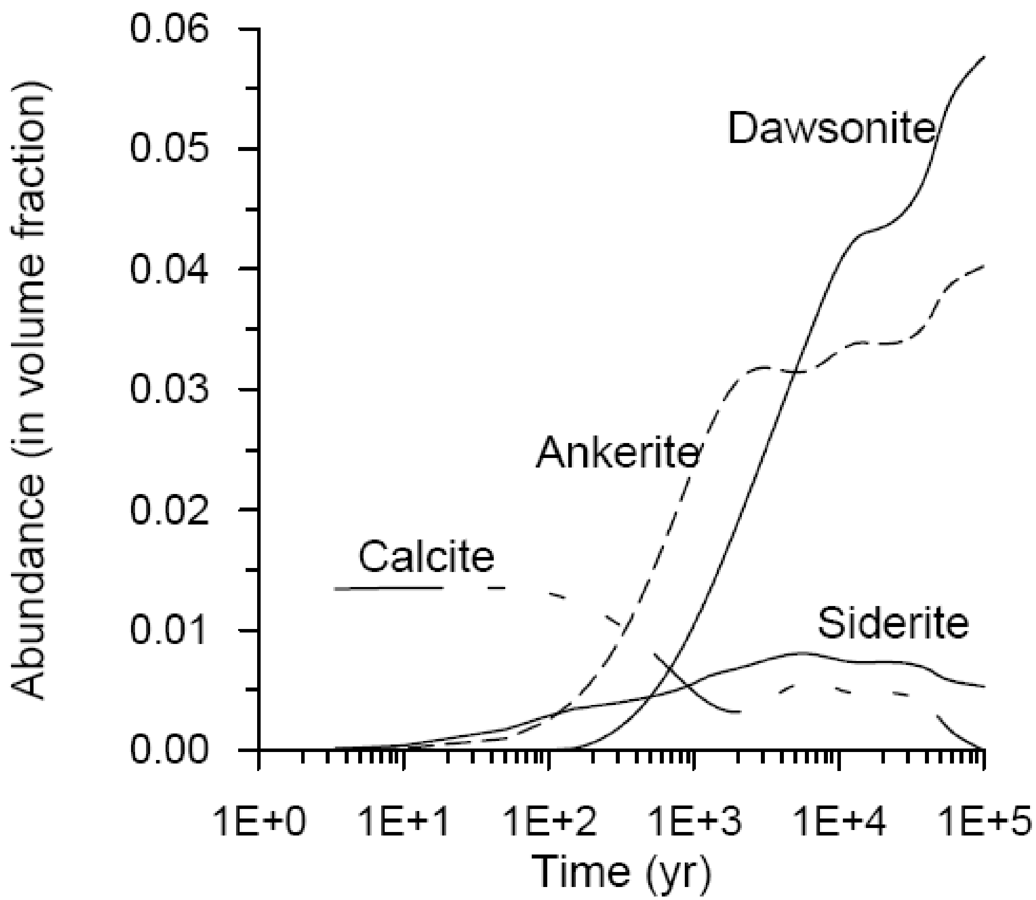
Southwest Regional Partnership on Carbon Sequestration

These do not include mineralization in spent oil shale retorts

There is enough porosity generated to store CO_2 generated from production

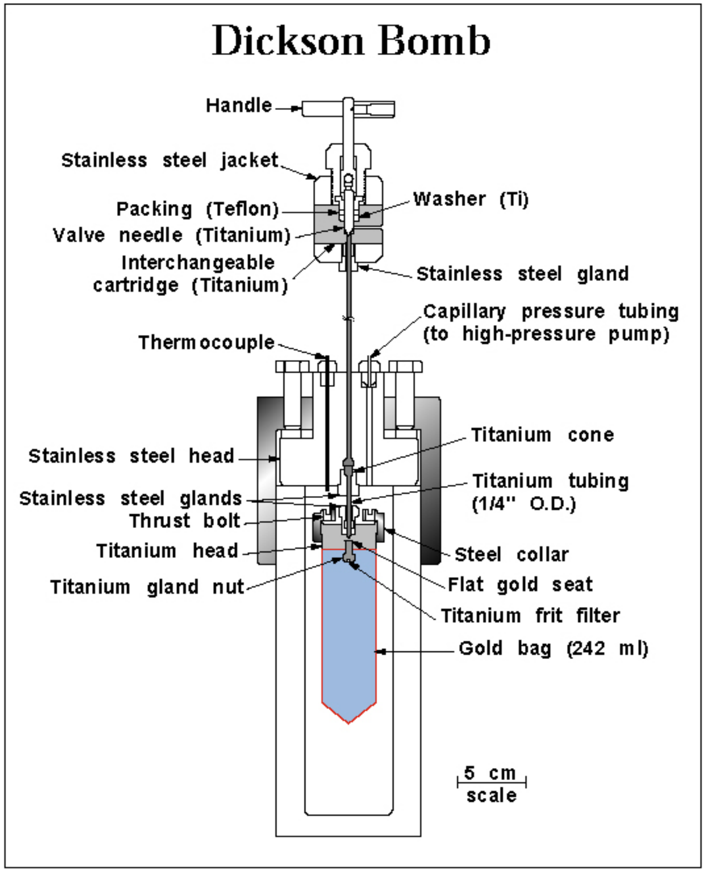
- 27 gal/ton at 75% Fischer Assay = 0.48 bbl/ton
- 70 kg CO_2/bbl of oil ⇒ 34 kg CO_2/ton of oil shale processed
- If converted to calcite, it would constitute 9 wt% of the retorted shale
- Kerogen is about 1/3rd of the rock volume
  - Pyrolysis removes 2/3rd of organic matter
  - The density of the remaining char is higher due to lower hydrogen content, but the char is microporous
  - There is some initial porosity, depending on sample
  - Porosity after retorting is ~30%
- Compaction might reduce porosity to ~20%
  - Carbonate mineralization would take ~half the available porosity

Mineralization reactions have been studied for injection of CO_2 into sandstones



- Mineralization depends on mutual diffusion of cations and CO_2 between the shale and neighboring sandstone
- Reaction times are slow because of low temperatures
- Calculations by Pruess at LBL

LLNL is studying mineralization reactions relevant to spent-retort conditions



Dickson bomb schematic

- Reactions run at 250 to 300 ^{o}C using retorted shale and realistic brine-CO_2 fluids
- Minerology determined by XRD, SEM, and EDS
- Reaction progress and equilibrium geochemical models used to understand the extent of CO_2 mineralization reactions

We will develop our CO_2 options over the next year

- Determine whether thermodynamic and kinetic conditions make CO_2 mineralization in spent retorts a viable option
  - Field test opportunities exist in late 2010 (end of pilot) and late 2013-early 2014 (end of semi-works)
- Determine whether there are any viable nearby markets for use in CO_2-EOR
- If neither of these options appears viable, seek a deep-injection sequestration option