CO_2 Mineral Sequestration Studies

Introduction, Issues and Plans

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Workshop on CO_2 Sequestration with Minerals
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Mineral Sequestration Program

Research effort seeks to refine and validate a promising CO_2 sequestration technology option, mineral sequestration also known as mineral carbonation

Goals:

- Understand the fundamental mechanisms involved in mineral carbonation
- Generate data to support process development
- Operate continuous, integrated small-scale process unit to support design

Current Partnerships

In order to effectively develop Mineral Sequestration, a multi-laboratory Working Group was formed in the Summer of 1998, participants include:

- Albany Research Center
- Arizona State University
- Los Alamos National Laboratory
- National Energy Technology Laboratory
- Science Applications International Corp.

What is Mineral Carbonation

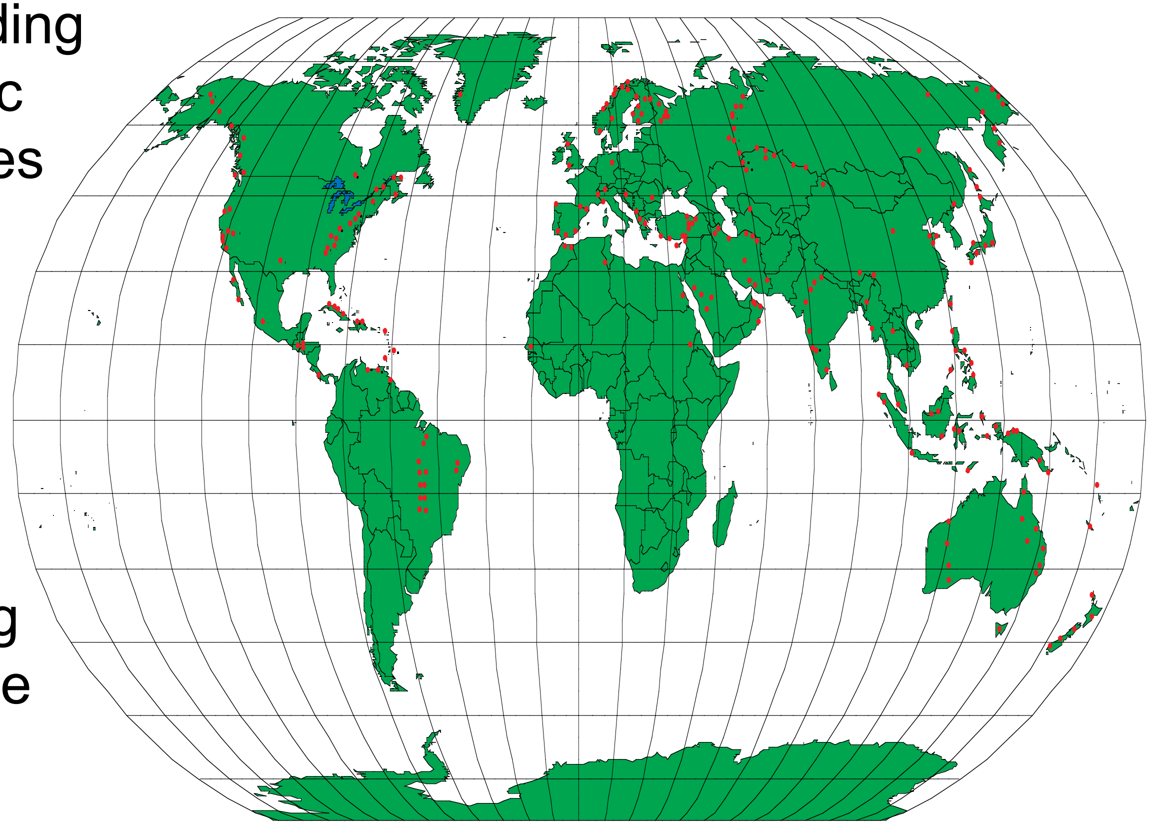
- **Reaction of CO_2 with Mg or Ca containing minerals to form carbonates**
- **Lowest energy state of carbon is a carbonate and not CO_2**
- **Occurs naturally in nature as weathering of rock**
- **Candidate Materials:**
  - Magnesium Silicates
  - Calcium Silicates
  - Industrial residues

Advantages of Mineral Carbonation

Vast capacity - deposits of ultramafic rocks exceeding even the most optimistic estimate of coal reserves

Readily accessible - near major high density power generation centers

No legacy issues - Long term stability unarguable naturally occurring and benign products



Carbonation Reaction Paths

Generalized reaction:

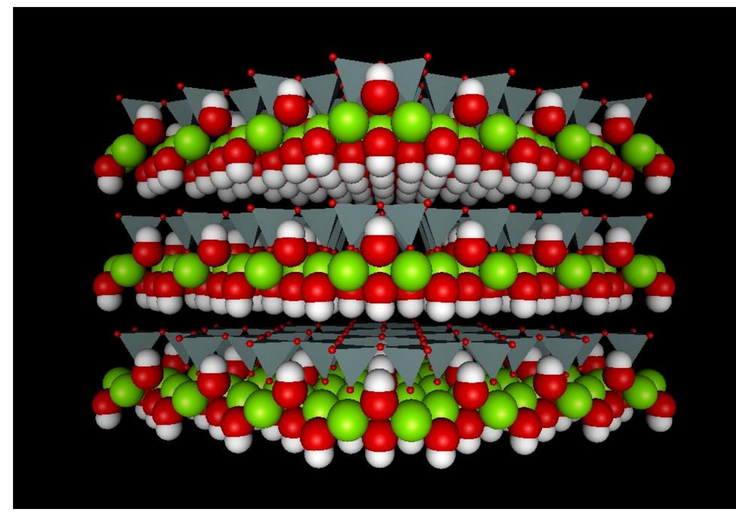
- $(Mg, Ca)_xSi_yO_{x+2y+z}H_{2z} + xCO_2 \rightarrow x(Mg,Ca)CO_3 + ySiO_2 + zH_2O$

Serpentine:

- $Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$
  - (MgO) = 38-45 wt pct (actual)
  - (Iron oxides) = 5-8 wt pct
  - (Water) = 13wt pct
- Exothermic reaction: **+** 64 kJ/mole
- One ton to dispose of 1/2 ton of CO2

Olivine (Primary mineral forsterite):

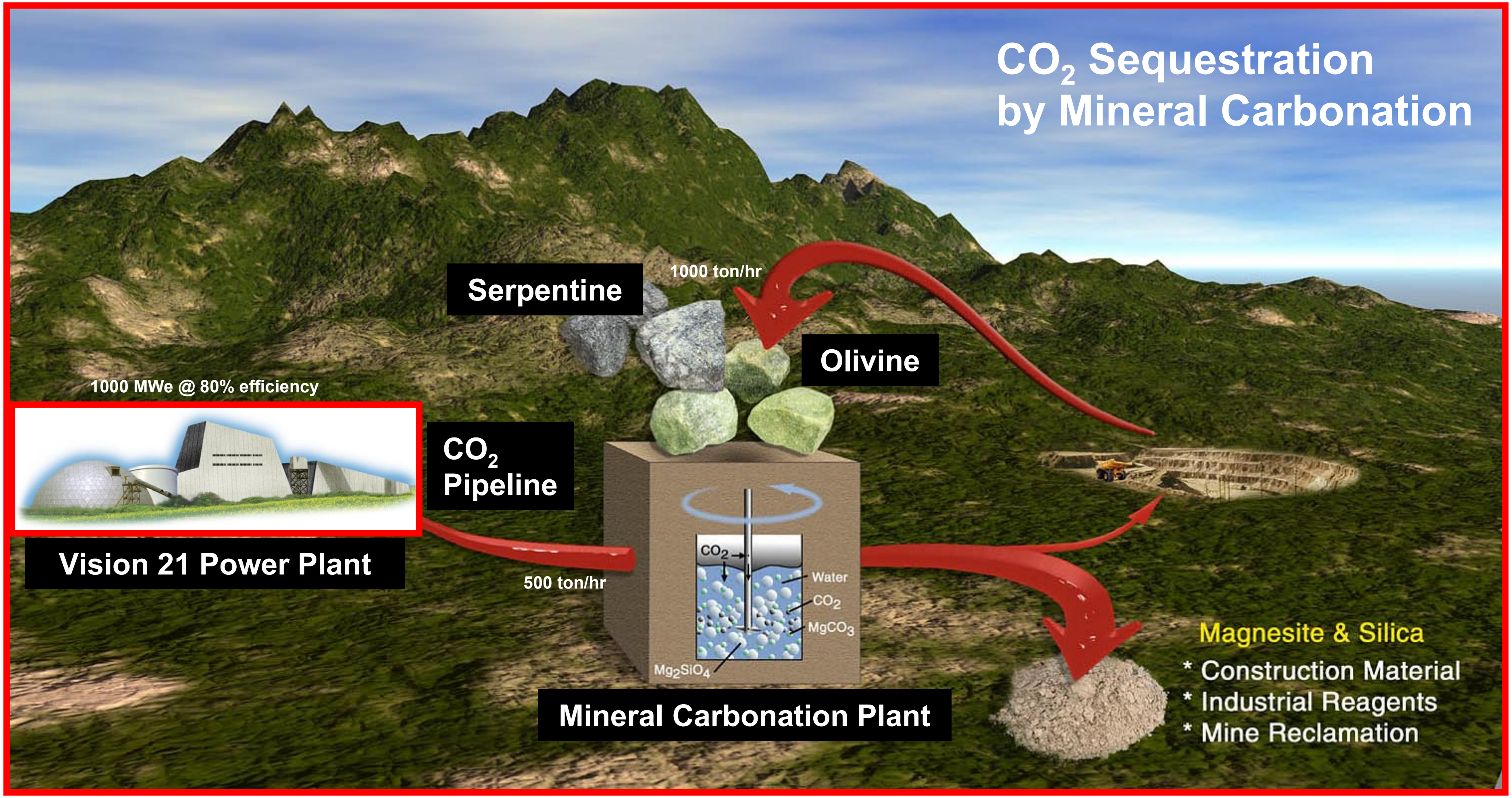
- $Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$
  - (MgO) = 45-50 wt pct (actual)
  - (Iron oxides) = 6-10 wt pct
- Exothermic reaction: + 95 kJ/mole
- One ton to dispose of 2/3 ton of CO2



Structural model of Serpentine (Lizardite)

NETL

Mineral Sequestration Concept



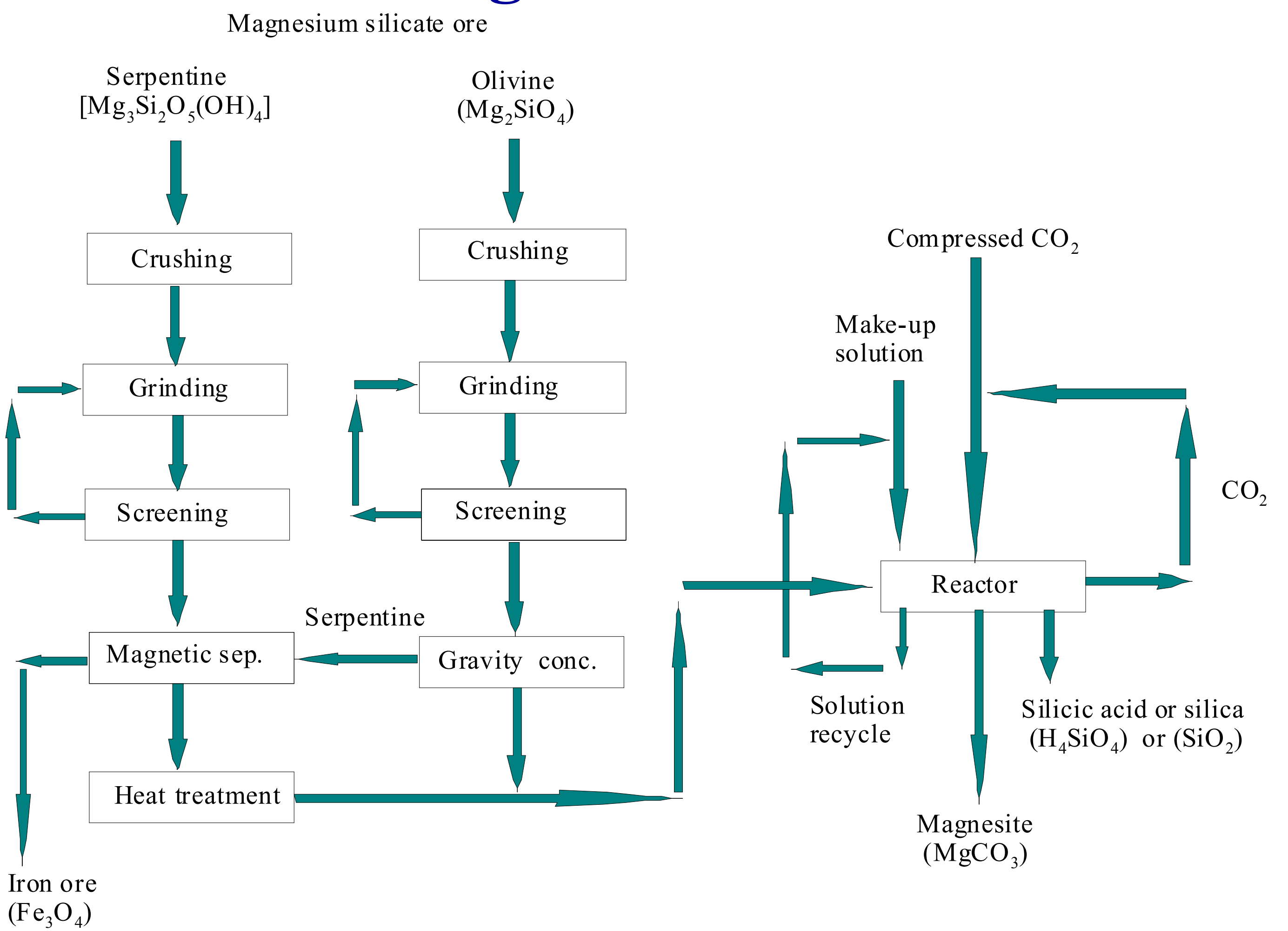
Courtesy of Albany Research Center

Issues Related to Mining and Milling Evaluated

- **Serpentine mines common**
  - road base & asphalt
  - additional capacity would be required
- **Scale of mining operations consistent with requirements**
  - 1000 tpd avg. (450 MWe, 35%, 24hr)
- **Mining costs of $3 - $5/ton**
- **Olivine used for refractories and foundry sand**
  - global resources not well characterized

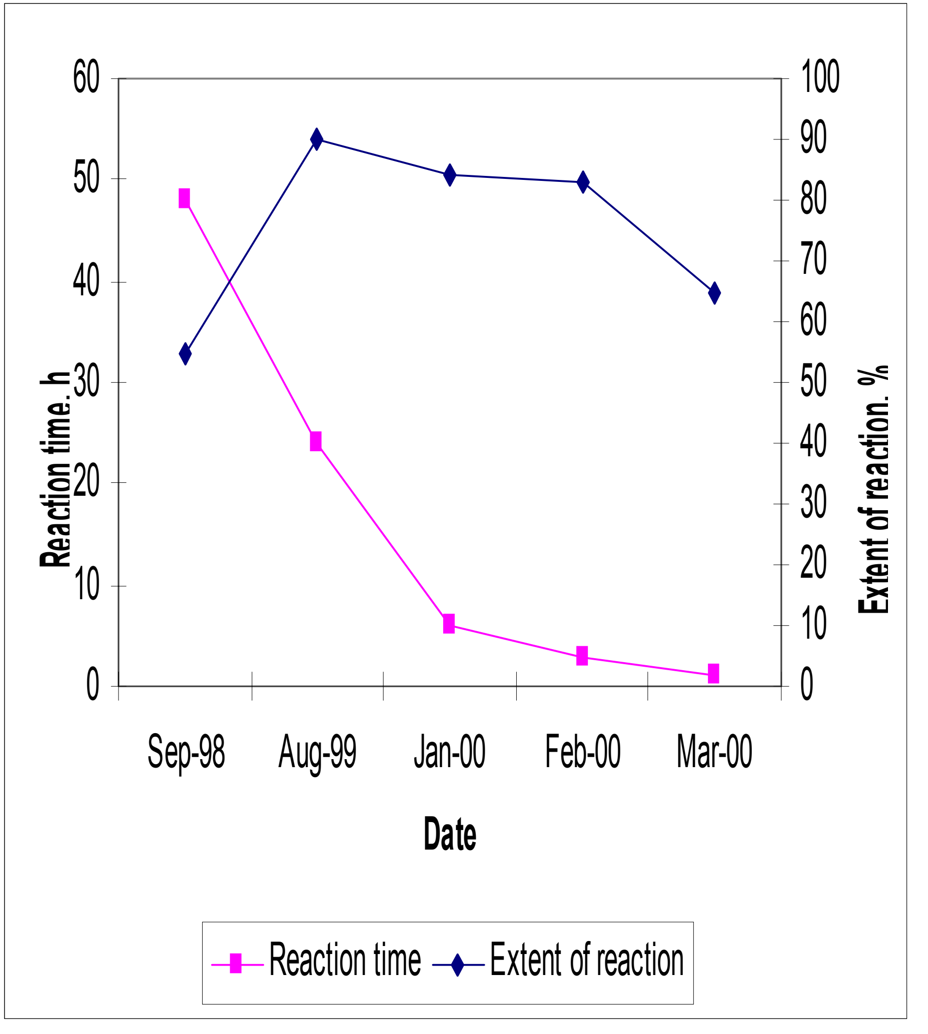
NETL

Magnesium Silicate Process Flow Diagram



Reaction Rate Increased by 10 Fold

- **Improvement of reaction rate is achieved by**
  - Pre-treat serpentine to remove chemically-bonded water and create open structure (600-650 C)
  - Add sodium bicarbonate and NaCl solution as additives
  - Sodium bicarbonate increases HCO_3^- concentration
  - NaCl may help release Mg ions from silicate
  - 78% conversion can be achieved in 30 minutes at 185 bar, & 155 ^{0}C
  -



Critical Issues

- <u>Pretreatment Issues</u> which includes mining of minerals and preparation of solid, gaseous or liquid feedstocks
- <u>Carbonation Reaction</u> which includes mechanisms and reactor designs
- <u>Post-Treatment Issues</u> which includes separation of carbonation products, and disposal of process effluents
- <u>Engineering Design, Assessment and Integration Activities</u> which includes process integration, cost estimation, etc.

Critical Issues

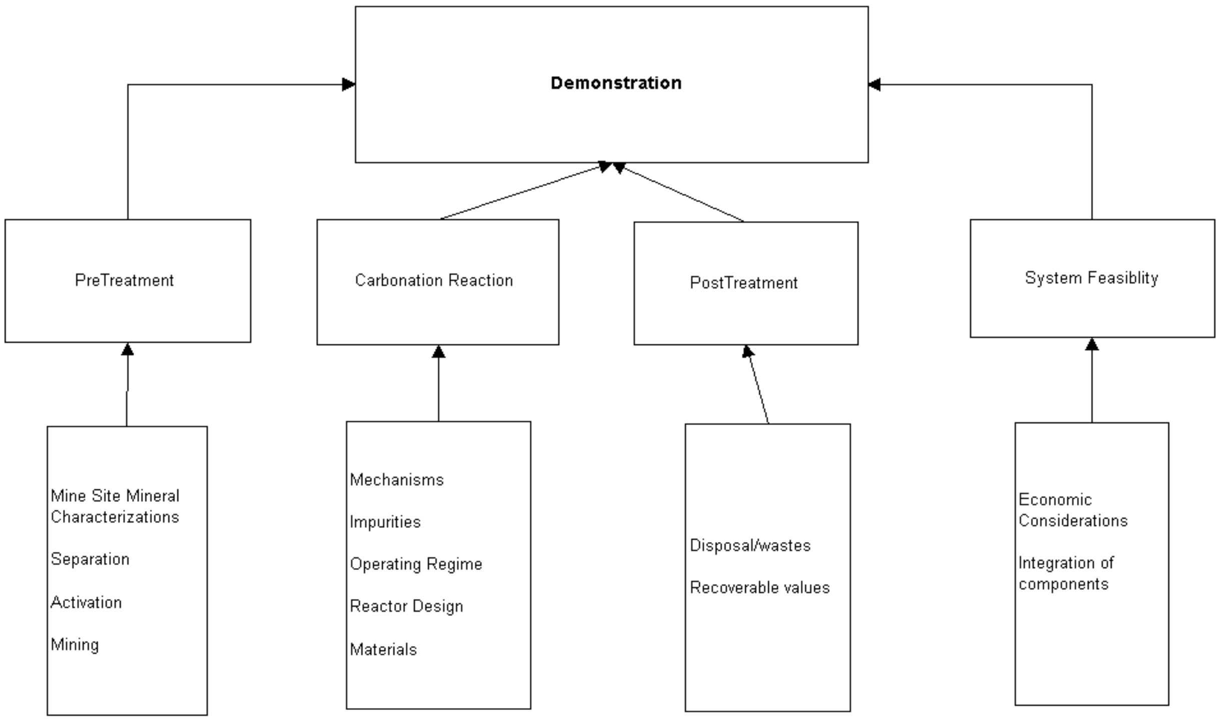


Figure X

Pretreatment Issues

- Sample Collection and Distribution
- Evaluate Effectiveness of Ore Impurities and Ore Pretreatment
- Evaluate the Effectiveness of Thermal and Chemical Mineral Pretreatment Processes
- Examination of two-step processes and the use of Alternate Feedstocks

Carbonation Reaction

- Construction of Additional Laboratory-Scale Reactors
- Temperature, Pressure & Solution Chemistry Effects
- Fundamental Support (e.g., modeling and data analysis)
- Construction & Operation of Continuous Bench-Scale Reactors

    Vertical two-phase bubble column Rx 10lb/hr rock

    Continuous processing unit 5 lb/hr rock

Post-Treatment Issues

- Characterization & Disposal of Affluent
- Recovery of Byproducts
- Testing of Separation

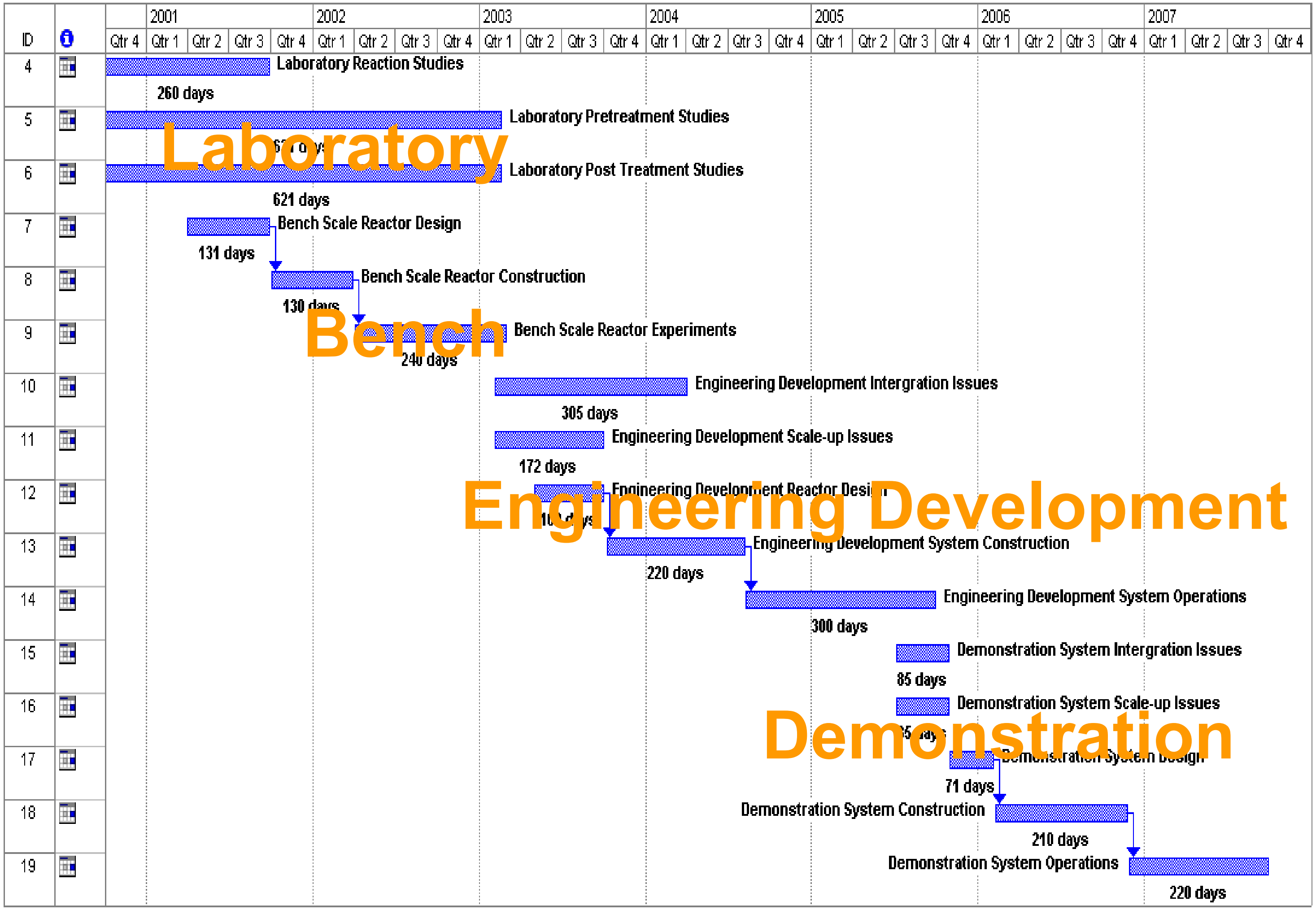
Engineering Design, Assessment and Integration Activities

- **Develop Carbonation Reactor Designs, Heat Exchanger Concepts and Balance of Plant Requirements**
- **Perform Cost Estimates, Sensitivity Studies and Life Cycle Analyses (LCA)**
- **Pilot Plant, Demonstration Plant and Preliminary Sequestration Plant Design and Cost Estimation Activities**
  - Construction & Operation of Integrated 500 lb/hr Carbonation Unit (1/2 MW)
  - Preliminary Design of 10MWe System

Design and assessment activities are necessary to continually evaluate process development requirements and guide R&D.

NETL

TimeLine



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4 Laboratory Reaction Studies 260 days
5 Laboratory Pretreatment Studies
Laboratory
6 Laboratory Post Treatment Studies 621 days
7 Bench Scale Reactor Design 131 days
8 Bench Scale Reactor Construction 130 days
9 Bench Scale Reactor Experiments
Bench
10 Engineering Development Intergration Issues 305 days
11 Engineering Development Scale-up Issues 172 days
12
Engineering Development
13 Engineering Development System Construction 220 days
14 Engineering Development System Operations 300 days
15 Demonstration System Intergration Issues 85 days
16 Demonstration System Scale-up Issues
Demonstration
17 71 days
18 Demonstration System Construction 210 days
19 Demonstration System Operations 220 days

Current Activities
FY 2001

- Gaining the mechanistic understanding required to identify a cost-effective carbonation route.
- Exploring promising two-step processes (i.e., separated dissolution and carbonation steps)
- Delineating operational parameters necessary to design a bench scale continuous reactor flexible
- Initiating an engineering assessment to establish an economic baseline and future research priorities.
- Pre- and post-treatment issues related to particle size effects, separation, crushing and grinding, by-product recovery, waste disposal, and thermal or chemical mineral treatments.

Near Term Activities
FY 2002

- Continue fundamentally oriented and applied laboratory carbonation studies
- Identify the most promising carbonation feedstock and route.
- Construction and operation of a continuous bench scale reactors, ARC and NETL
- Produce engineering data utilizing the 5 lb/hr bench scale carbonation reactor to evaluate potential operating characteristics
- Initiate by-product characterization and recovery
- Initiate studies on disposal of effluents

Future Program Activities

- 2003 - Initiate small pilot-scale testing to produce realistic engineering design data.
- 2005 - Complete technical and economic assessment and construct next-generation integrated pilot plant at relevant scale

Future Program Activities

- 2006- Design of a Demonstration scale unit will be completed
- 2007- Construction of the Demonstration scale carbonation system is completed and operation is begun