CO_2 Mineral Sequestration Studies in US

by

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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**
- **Already *proven* on large scale**
  - Carbonate formation linked to formation of the early atmosphere

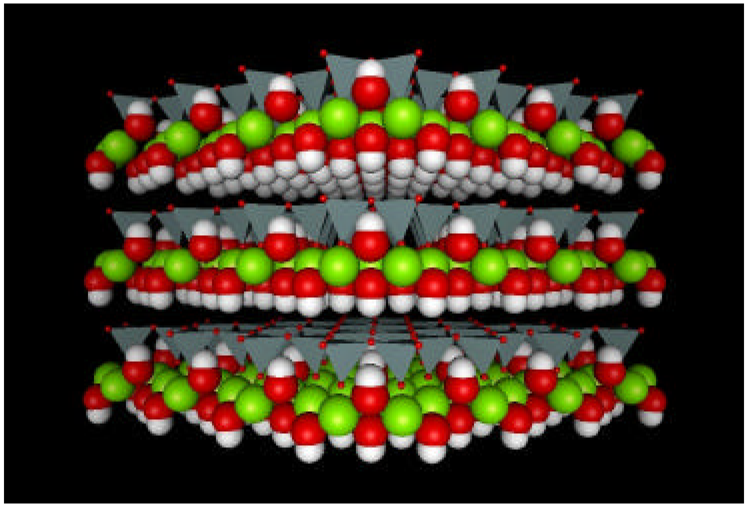
Global Carbonation Reaction Paths

Generalized reaction:

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

Serpentine:

- $Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$
- Exothermic reaction: + 64 kJ/mole
- One ton to dispose of 1/2 ton of CO2



Structural model of Serpentine (Lizardite)

Forsterite:

- $Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$
- Exothermic reaction: + 95 kJ/mole
- One ton to dispose of 2/3 ton of CO2

Advantages of Mineral Carbonation

- **Long term stability unarguable**
  - End product thermodynamically favored
  - No legacy issues
  - Naturally occurring and benign products
- **Ultramafic rocks are ubiquitous**
- **Potential to become economically viable**
  - Process is exothermic
  - Potential to produce value-added byproducts
  - Utilization/neutralization of wastes
- **Compatible with advanced fossil fuel power generation and coproduction concepts**
  - Process configuration and siting flexibility

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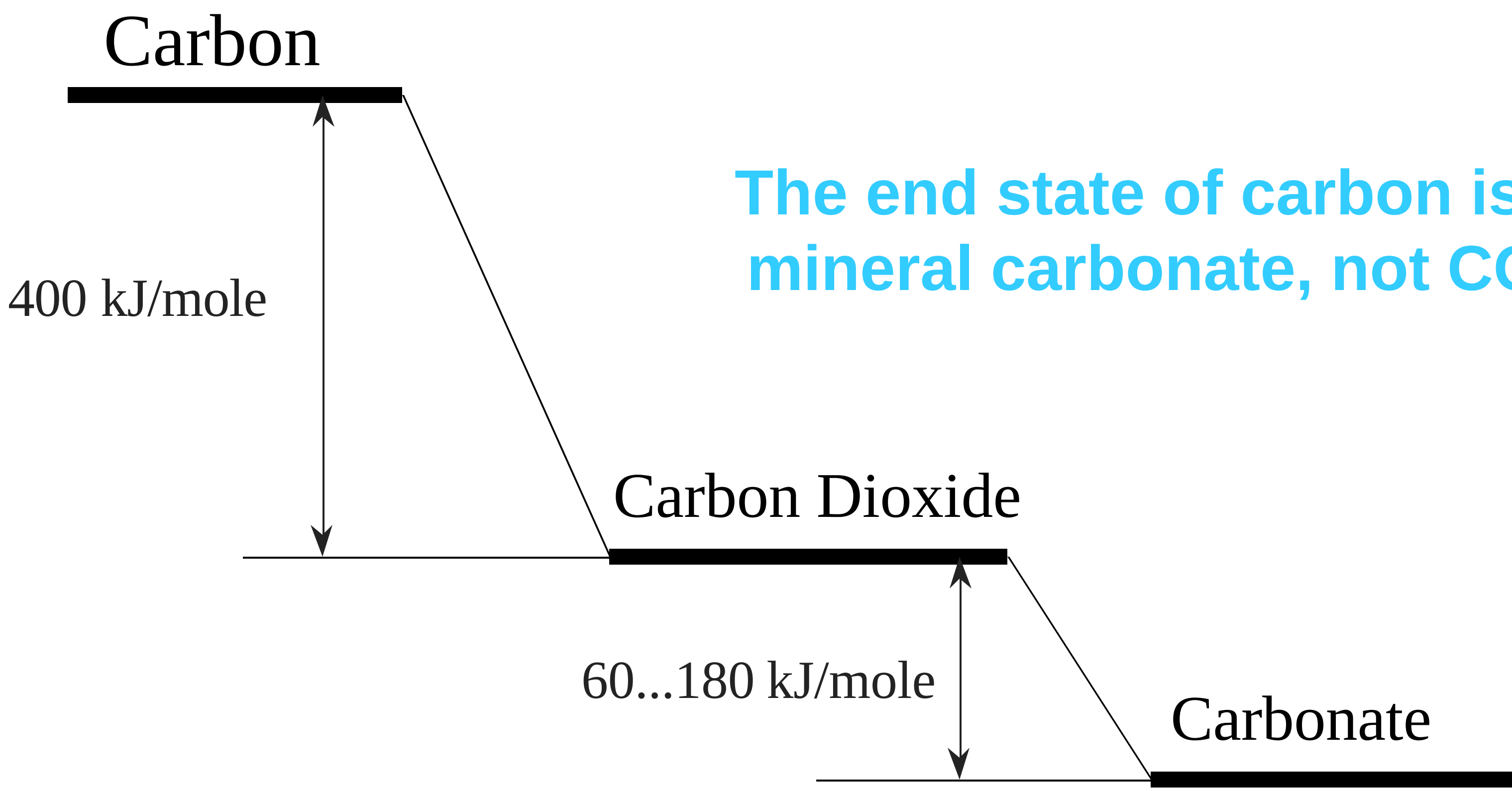
Carbonation Releases Energy



The end state of carbon is a mineral carbonate, not CO_2

CO_2 Storage Options

- **Many potential sequestration options available with large storage capacities**

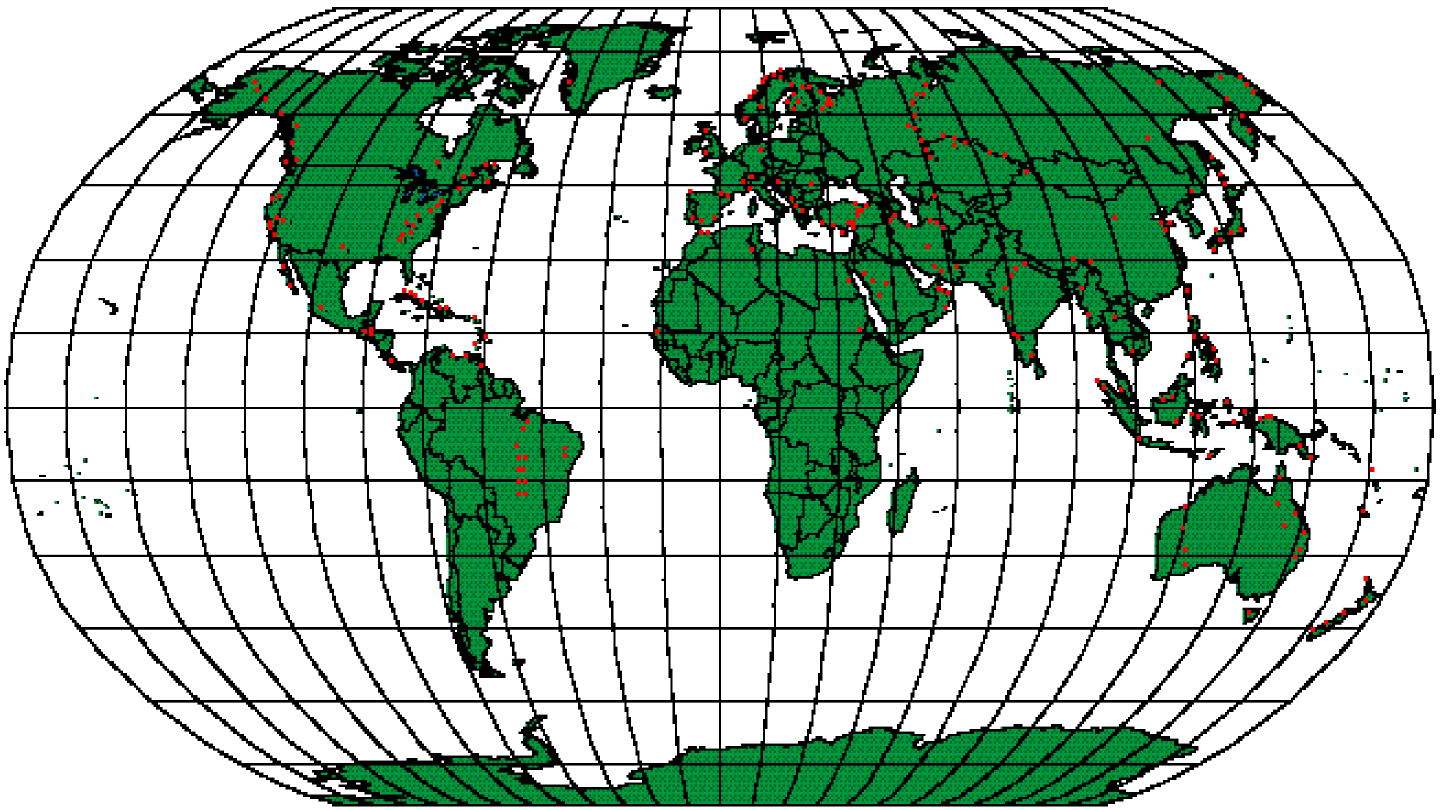
Worldwide CO_2 Storage Capacity[1]

Storage Option	Capacity (billions of ton)
Deep Ocean	5,100 - 100,000
Mineral Sequestration	**>>1,000**
Deep Aquifers	320 - 10,000
Depleted Oil Wells	500 - 1,000
Depleted Gas Reservoirs	150 - 700
Coal Seams	150 - ???
(Fossil Fuel Reserves ………. 3,500)	

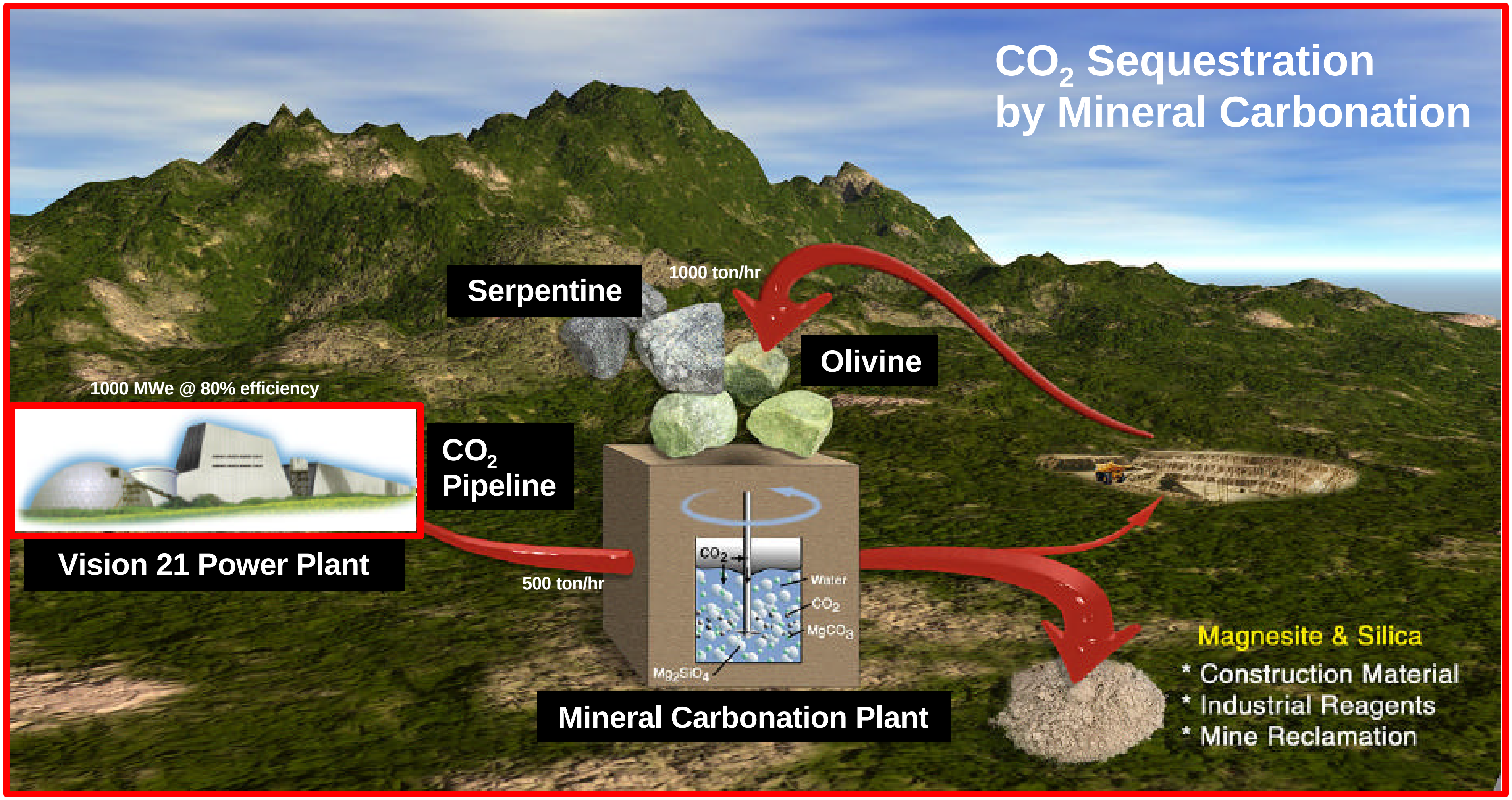
[1]Based on IEA/GHG & EIA/IEO 2000
[2] Est. of US capacity by Goff,et al, 2000

Vast Raw Material Deposits Worldwide

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



Mineral Sequestration Concept



Courtesy of Albany Research Center

Major Barriers and Challenges

- **Naturally occurring carbonation is a slow process, finding fast reaction routes is the key**
- **Mining, milling and related environmental issues must be addressed**
- **Although the carbonation reaction is exothermic, heat recovery may be challenging at low temperature levels**

Mineral Carbonation Program Goals

- **Generate data to support process development**
  - Conduct laboratory- and pilot-scale tests, examining:
    - Reaction pathways, including use of catalysts
    - Alternative feedstocks, e.g., minerals and residues
  - Consider environmental issues
- **Operate continuous, integrated small-scale process unit to support design**

Partnerships

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

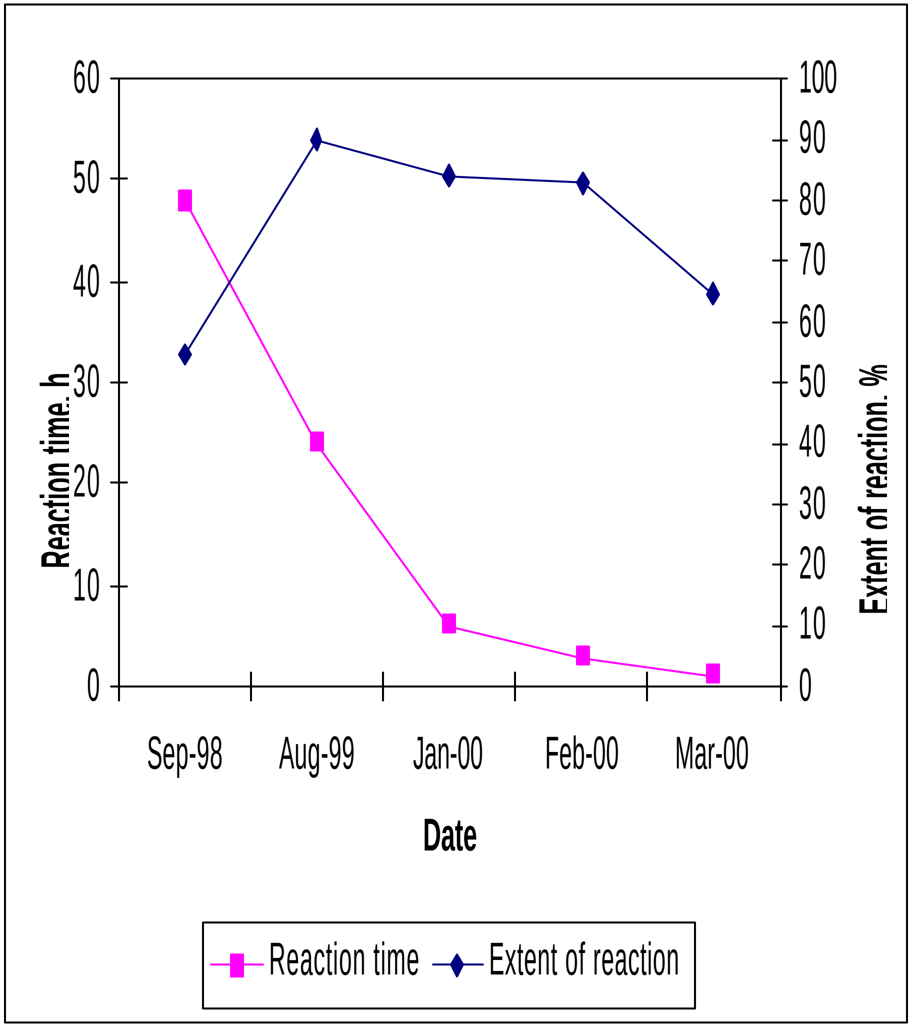
- Albany Research Center
- Arizona State University
- Los Alamos National Laboratory
- National Energy Technology Laboratory

Status of Research Effort

- **Preliminary evaluation of reaction paths**
  - Aqueous HCL process employing mineral-derived $Mg(OH)_2 + H_2O$ (found expensive)
  - $MgCl_2$ Molten Salt process (found unreactive)
  - Direct Carbonation using supercritical CO_2 and water at elevated pressures and temperatures (found promising)
- **Exploratory tests of direct carbonation run using mineral pretreatment and additives**
- **Initial mining survey completed**
- **Preliminary life cycle analysis, sensitivity study and economic assessment initiated**

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, and 155 ^{0}C**



Some Recent Mineral Carbonation Results

Min. Type	H.T	Temp. (C)	Pressure (Atm)	Time (Min)	Conv. (%)
O-40	---	185	115	360	84
O-112	---	155	150	60	33
S-83	CO_2	155	150	60	82
S-84	CO_2	155	185	30	78
S-99[1]	CO_2	155	150	60	79
S-100[1]	Air	155	150	60	79

[1] Tests using nonmagnetic serpentine fraction,

O - olivine, S-serpentine, H.T.-heat treatment gas

This is why Bill is smiling

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 not a barrier**
  - $3 - $5/ton

Analyzing Molecular Changes in Carbonation Reactions

- **In-situ TEM pictures at the Arizona State Univ. reveal that dehydroxylation is intimately associated with carbonation of $Mg(OH)_2$**
- **Study is planned to evaluate the structural changes of serpentine**
- **Use of synchrotron radiation source to monitor real-time structural changes of serpentine/olivine to carbonates in solution is planned**

Near-Term Activities

- **Improve direct carbonation process**
  - Continue autoclave tests, modifying solution chemistry, examine promoters and catalysts
  - Increase support for fundamental lab. studies to identify mechanisms and opportunities
  - Look for tie-ins with geologic sequestration
- **Identify and test alternative high volume residues - feedstocks such as flyash**
- **Initiate LCA/economic feasibility studies examining costs and potential environmental impacts**
- **Increase outreach to industry and the scientific community**

Continue Improving Carbonation Reaction Rate

- **Examine the roles of additives in helping dissolve CO_2 in solution, and release Mg ions from the mineral crystal structure**

- **Identify and test new additives and pretreatment methods**

- **Planned continuous examination of crystal structure changes in reaction cell using synchrotron radiation source**

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Test Fly Ash and Other Waste Streams

- **Some fly ash has high CaO and MgO concentration**
- **Less processing may be needed**
  - Mining minimal
  - Fine particle sizes
- **Potential to react with CO_2 at lower pressure than Mg silicates**
- **Likely to be implemented earlier than olivine/serpentine process if economics are more favorable**

Relation with Geological Sequestration

- **A thorough understanding of the reaction chemistry of CO_2, water, and minerals under elevated pressure is necessary to understand the long-term behavior of CO_2 injection in geologic formations**

- **The knowledge gained in this program may help design systems employing direct injection of CO_2 into underground formations to form carbonates**

Program Schedule - I

- Pre 2000 - Identify most promising mineral carbonation process and focus on process optimization
- 2000 - Bring additional autoclave facilities into operation and test coal ash and other residues
- 2001 - Initiate advanced carbonation reaction, and by-products studies. Begin system design and integration effort

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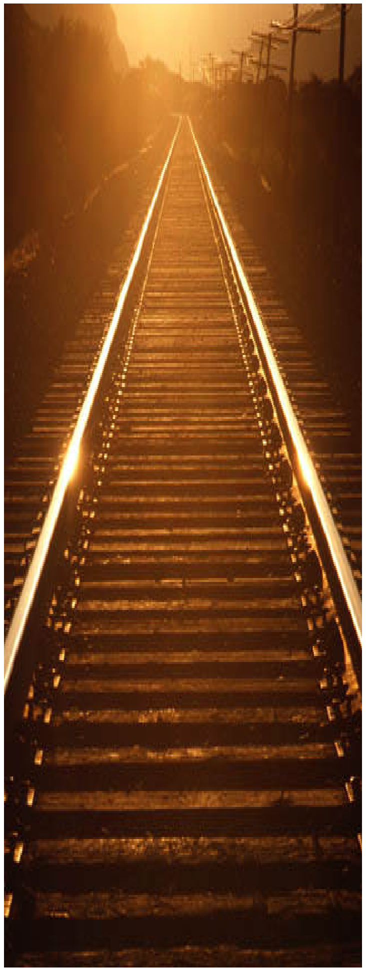
Program Schedule - II

- **2002 - Complete design of flexible pilot-scale carbonation and by-product recovery facilities**
- **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**



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