Mineral Sequestration Utilizing Industrial By-Products, Residues, and Minerals

Daniel J. Fauth and Yee Soong
U.S. Department of Energy
National Energy Technology Laboratory
Pittsburgh PA, 15236-0940

Mineral Sequestration Workshop
National Energy Technology Laboratory
August 8, 2001

Overview

- **Introduction**
  - Objective
  - Goals
  - NETL Facilities
- **Effect of Solution Chemistry on Carbonation Efficiency**
  - Buffered Solution + NaCl
  - Buffered Solution + MEA
- **Effect of Pretreatment on Carbonation Efficiency**
  - Thermal Treatments
  - Chemical Treatments
- **Carbonation Reaction with Ultramafic Minerals**
  - Serpentine
  - Olivine

Overview

- **Carbonation Reaction with Industrial By-products**
  - Fly Ash
    - Freeman United Coal
    - Consol Energy - Spray Dryer Ash
  - Dravo Lime Co (Carmeuse NA) By-product
    - Dravo By-product A
    - Dravo By-product B
    - Dravo By-product A & B + Olivine
    - Dravo By-product B + HT-Serpentine

Carbon Sequestration Science Focus Area

- DOE's Mineral Sequestration Program, managed by NETL, will provide a long-range options for drastically reducing CO_2 emissions from fossil-fuel-fired heat and power facilities. The Program encompasses research and field testing of a wide range of carbon sequestration options geologic, oceanic, terrestrial, and other innovative approaches (Mineral Sequestration). Successful deployment of these options will enable the continued use of low-cost and plentiful fossil energy resources and help stabilize the increased greenhouse gas concentrations in the atmosphere. Overall, this Program, of which the Carbon Sequestration Science Focus Area is a part, seeks to develop options for sequestering significant amounts of carbon by 2025.

NETL

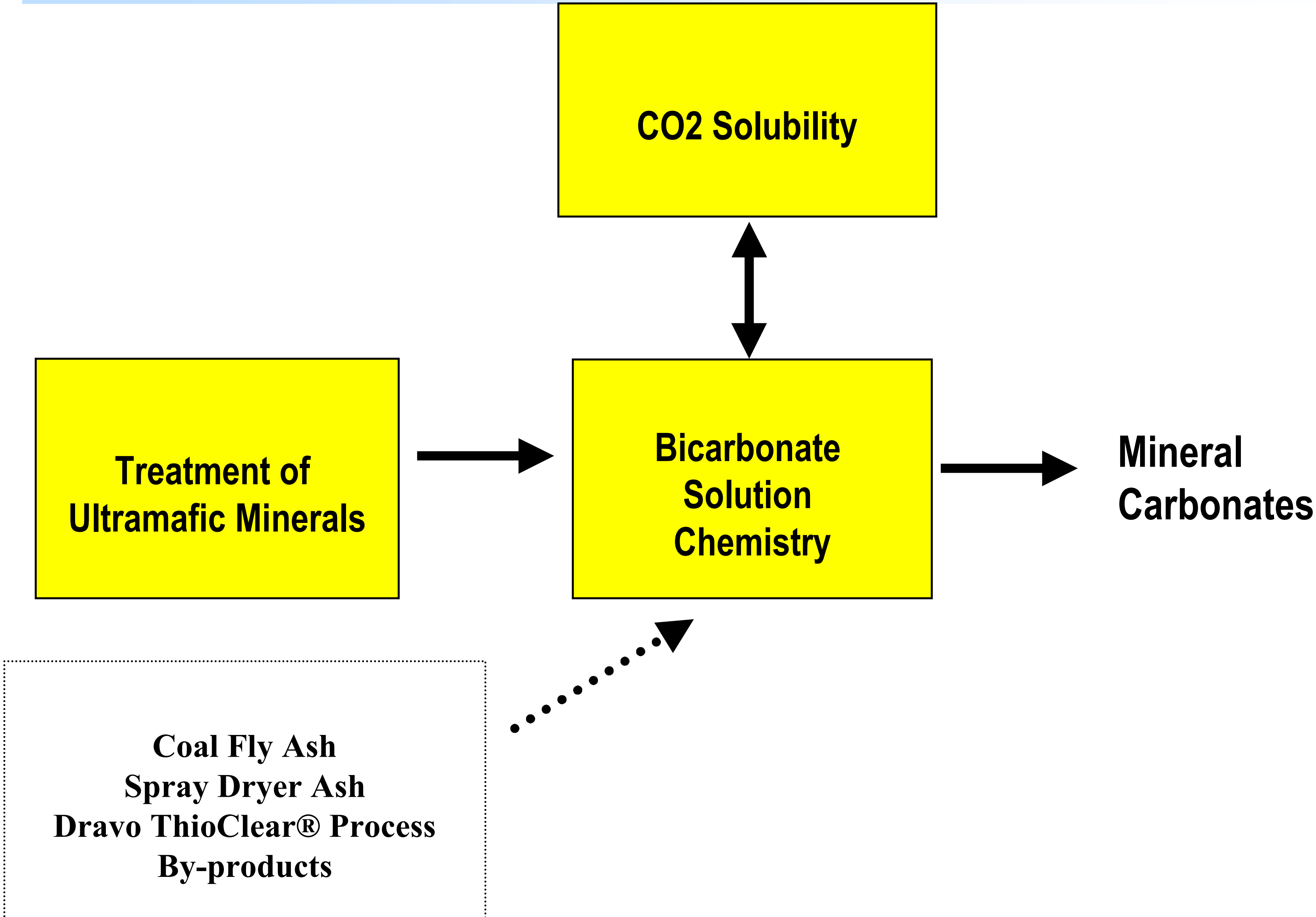
Capturing Carbon Dioxide as Mineral Carbonates

- **Primary Focus:** The ability to capture and store CO_2 emitted by fossil fuel-fired power stations and other industries could help maintain the uninterrupted use of U.S. fossil energy reservoirs well into the 21st century. In the Mineral Carbonation Study Program, NETL has focused part of its research efforts on developing a long-term mitigation strategy for large-scale reduction of CO_2 as stable mineral carbonates. Developing a useful knowledge base of mineral sequestration is important to understand the potential impact and economic viability of carbon management related processes.

NETL

Mineral Sequestration - NETL Facilities

- **NETL 1-Liter CSTR Facility**
  - Unit consists of four parts:
    - Hastelloy C-2000 pressure vessel
    - Electric furnace, external jacket type
    - MagneDrive II magnetically actuated rotary impeller system
- **NETL 500-mL CSTR Facility**
  - Unit consists of six parts:
    - Hastelloy C-276 pressure vessel
    - Electric furnace, external jacket type
    - Low temperature electric furnace, O-ring sealed with water cooled jacket
    - Dyna/Mag magnetic drive mixer with gaspersator agitator
    - ISCO CO_2pump with controller and temperature jacket
    - Computer control and data acquisition system

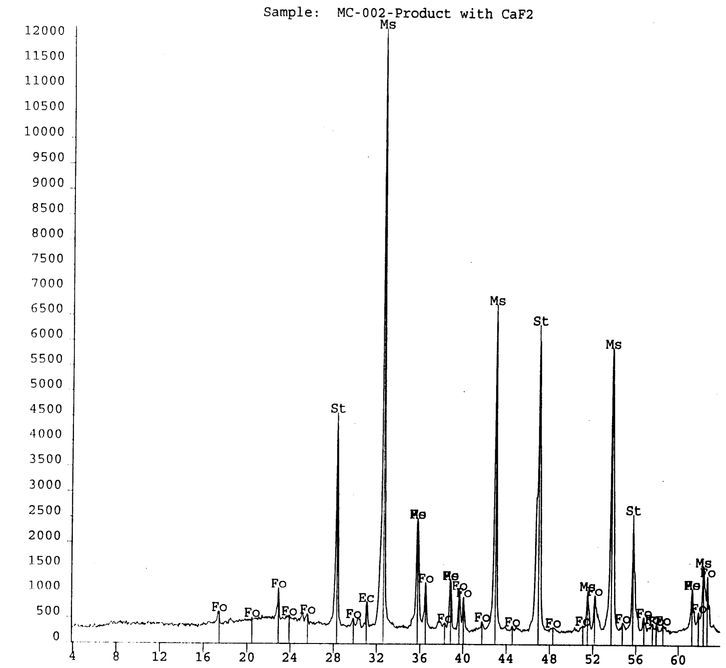

CO2 Solubility
Treatment of Ultramafic Minerals
Bicarbonate Solution Chemistry
Mineral Carbonates
Coal Fly Ash
Spray Dryer Ash
Dravo ThioClear® Process
By-products

Scanning electron micrograph
for Olivine carbonation product - $MgCO_3$

Experimental Mineral reactants, olivine (Mg_2SiO_4) and serpentine [$Mg_3Si_2O_5(OH)_4$] and their respective post-carbonation solid samples were characterized for their chemical composition and surface morphology using techniques such as ICP-AES, XRD, XPS, and SEM-EDX. Investigation into the carbonation characteristics of these mineral reactants under fixed conditions of pressure, temperature, bicarbonate solution chemistry, and pre-treatments were performed utilizing a continuous-stirred-tank-reactor (CSTR). Coal fly ashes was also investigated. Calculation of magnesium carbonate yields was based on the concentration of MgO within the starting reactants (olivine, serpentine) and the stoichiometry of reaction(s) listed below.

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$$

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3\,MgCO_3 + 2SiO_2 + 2H_2O$$

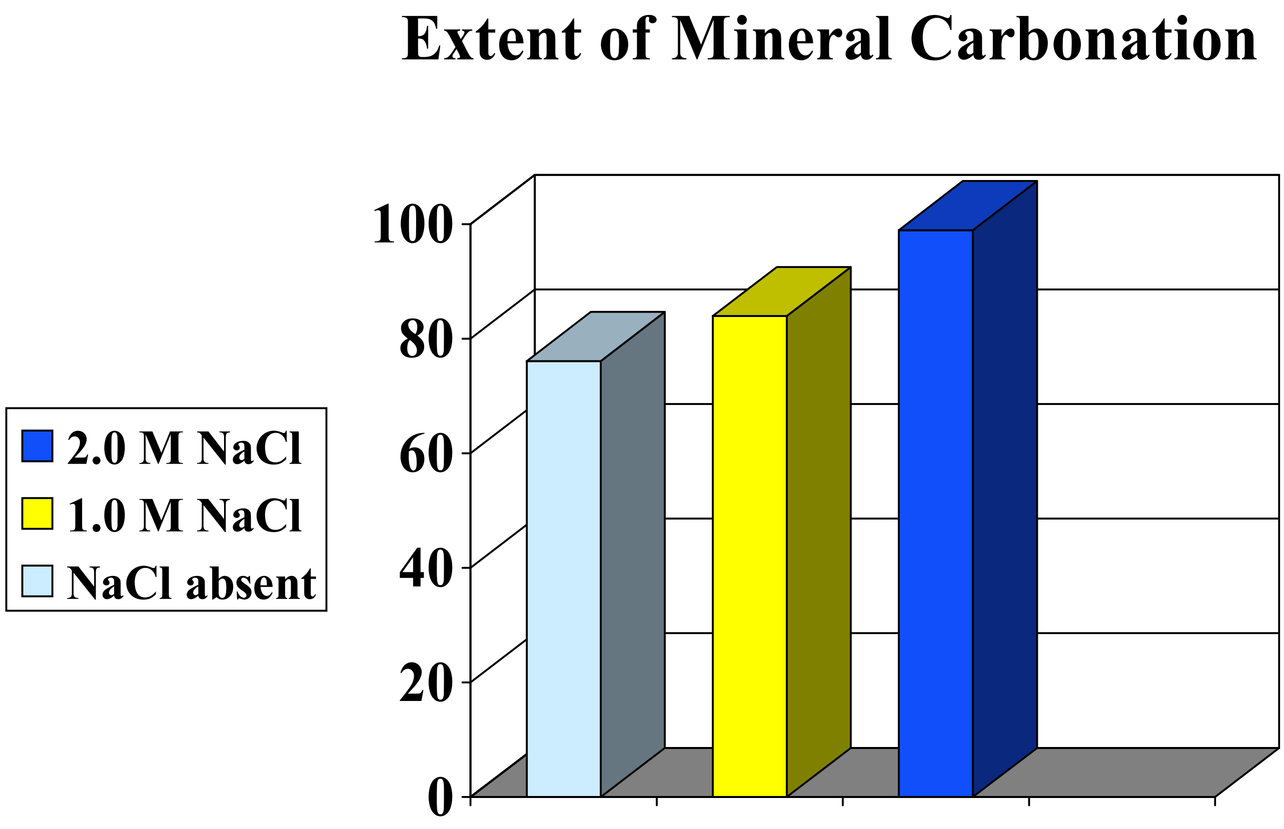


X-ray diffraction pattern for Olivine carbonation product

Pattern scheme: magnesite (Ms), forsterite (Fo), enstatite (Ec),

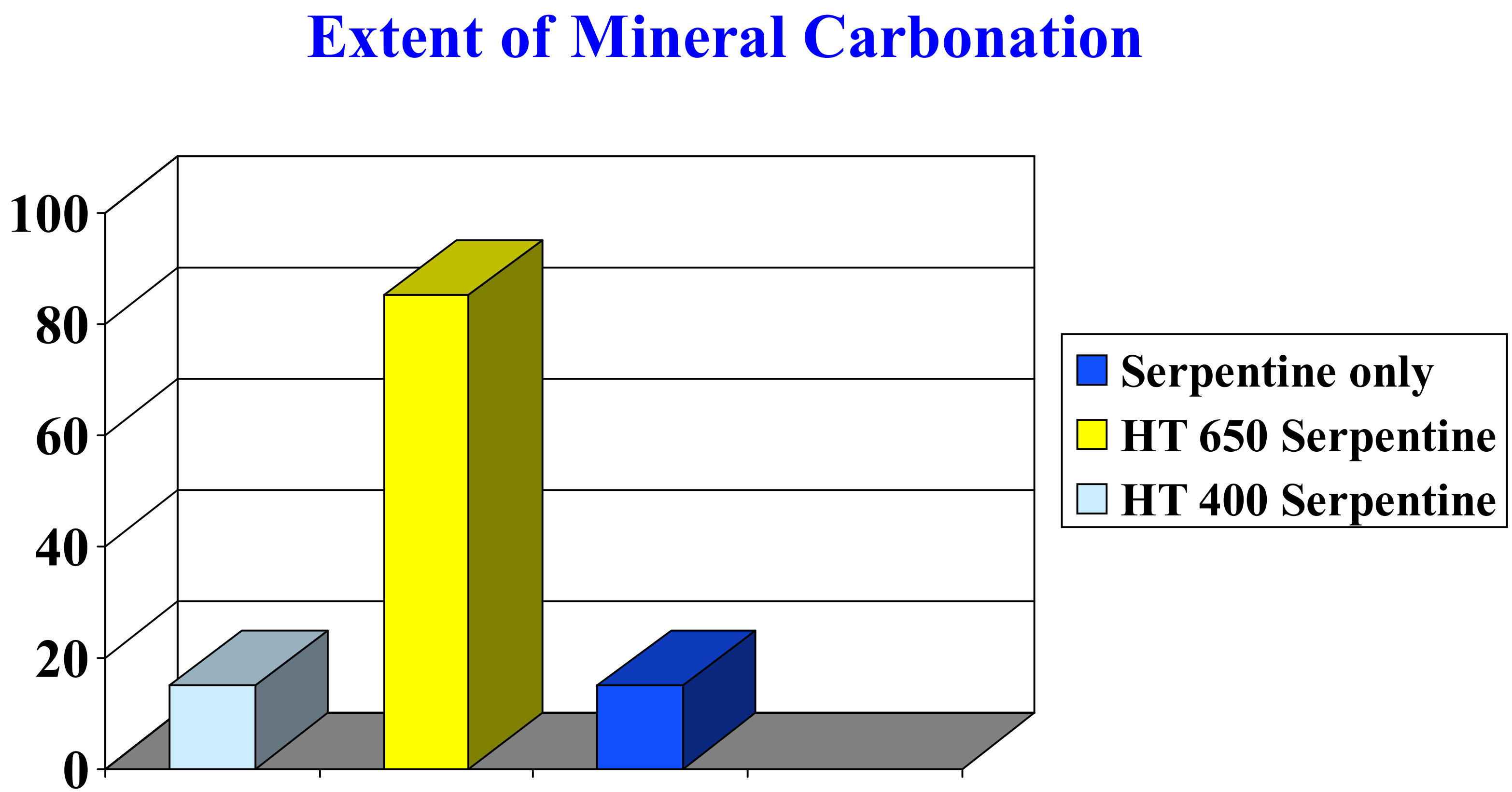
Result: Identification of magnesite ($MgCO_3$) as the primary phase in the solid mineral carbonation reaction products.

Effect of Solution Chemistry on Carbonation Efficiency



Reactant: Olivine, Twin Sisters Range, Washington, USA
Bicarbonate Solution: 0.5 M Na_2CO_3; 0.5 M $NaHCO_3$; *X*M NaCl
Temperature = 185°C; Pressure = 115 atms.; Time = 30 minutes

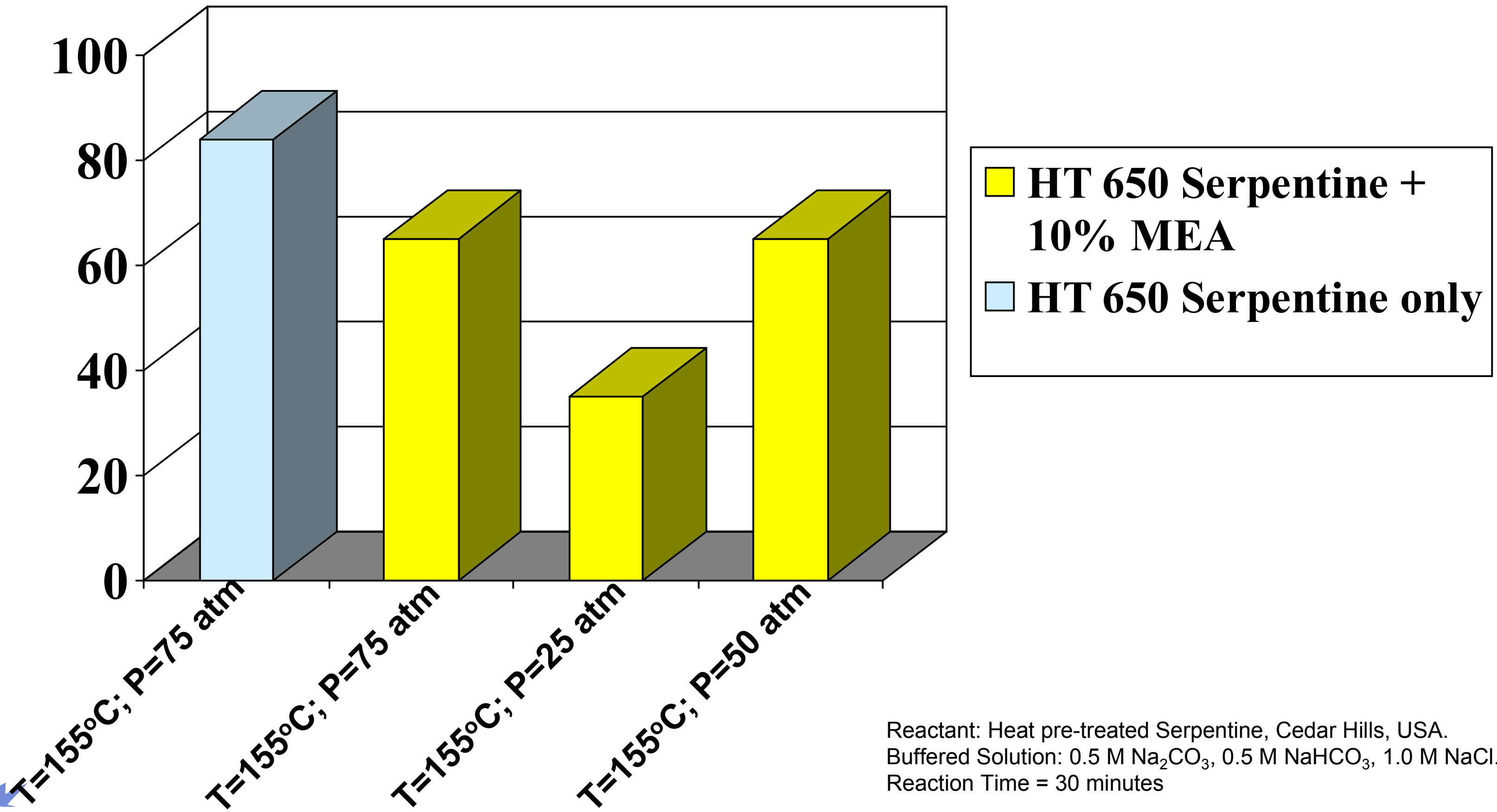
Serpentine Carbonation Efficiency -Effect of Thermal Pre-treatment



Reactant(s): Serpentine, Cedar Hills, PA/MD State Line District, USA . HT 650 Serpentine - Serpentine, Cedar Hills, PA/MD State Line District, USA thermally pre-treated @ 650ºC for 2 hours. HT 400 Serpentine - Serpentine, Cedar Hills PA/MD State Line District, USA ; thermally pre-treated @ 400ºC for 2 hours.Reaction Conditions: T = 155ºC, P_T = 75 atm, Reaction Time = 0.5 hrs. Buffered Solution: 0.5 M Na_2CO_3, 0.5 M $NaHCO_3$, 1.0 M NaCl

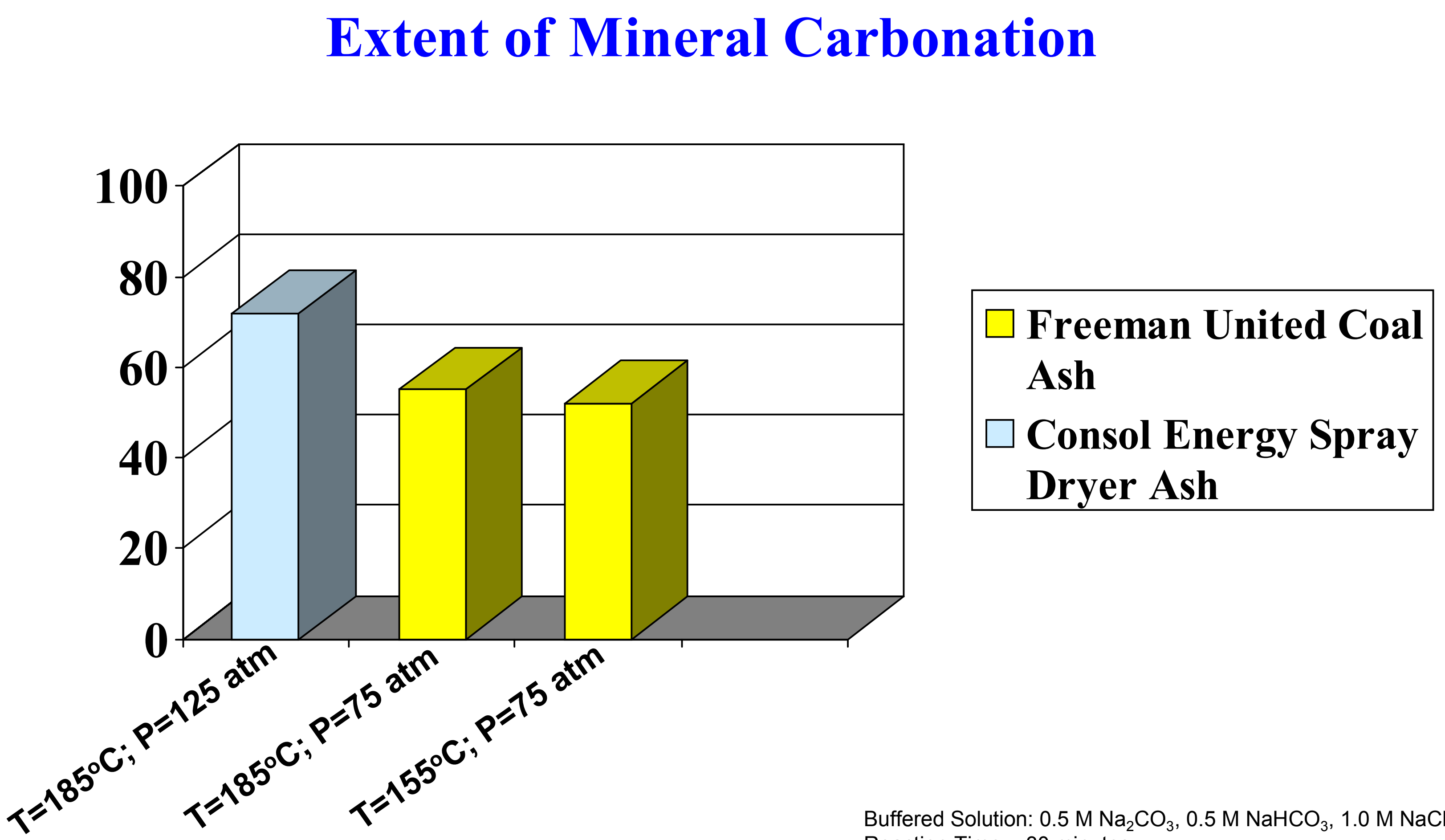
HT 650 Serpentine Carbonation Efficiency
Effect of MEA and Pressure

Extent of Mineral Carbonation



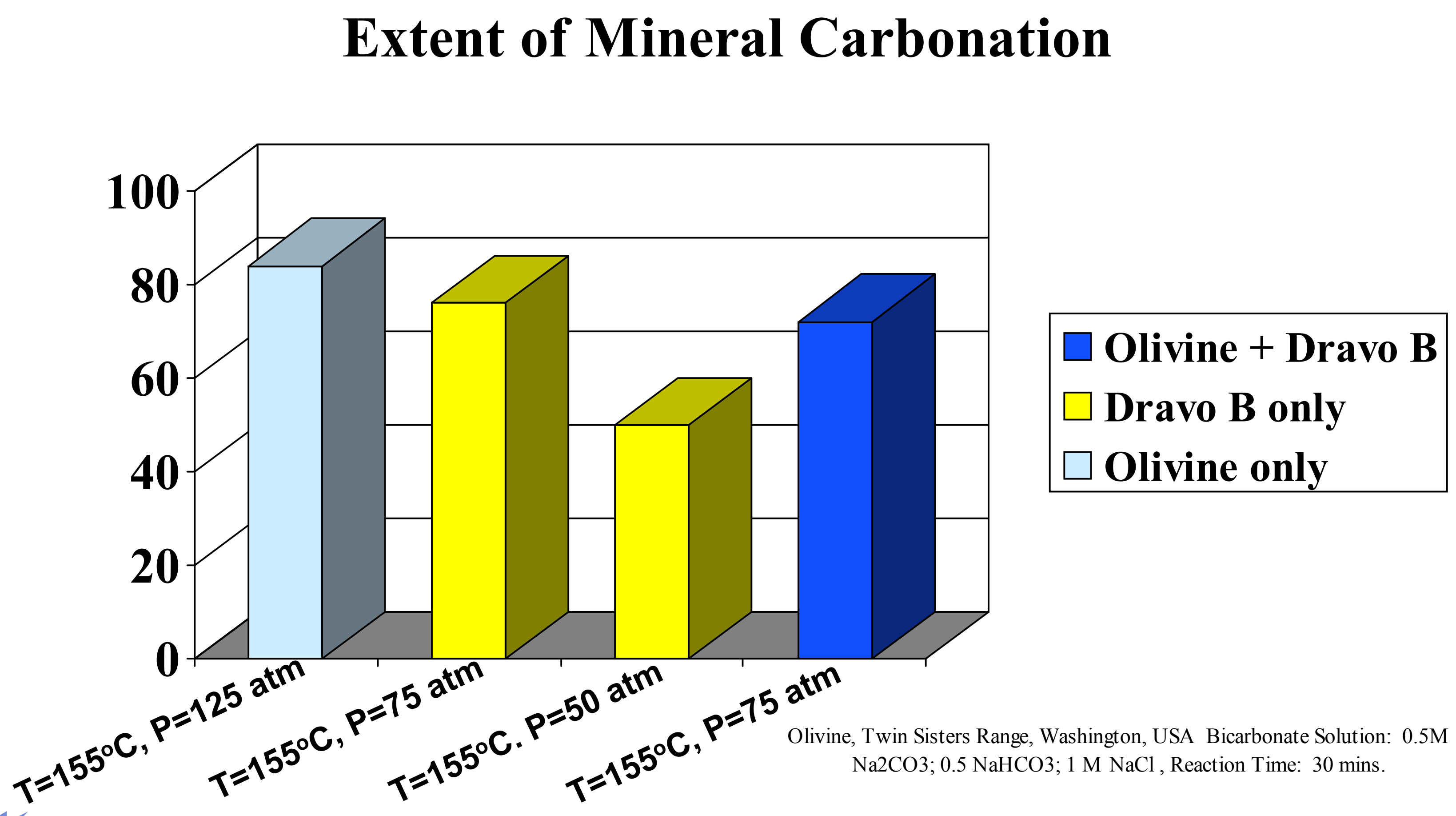
Reactant: Heat pre-treated Serpentine, Cedar Hills, USA.
Buffered Solution: 0.5 M Na_2CO_3, 0.5 M $NaHCO_3$, 1.0 M NaCl.
Reaction Time = 30 minutes

Carbonation Efficiency of Coal Fly Ash



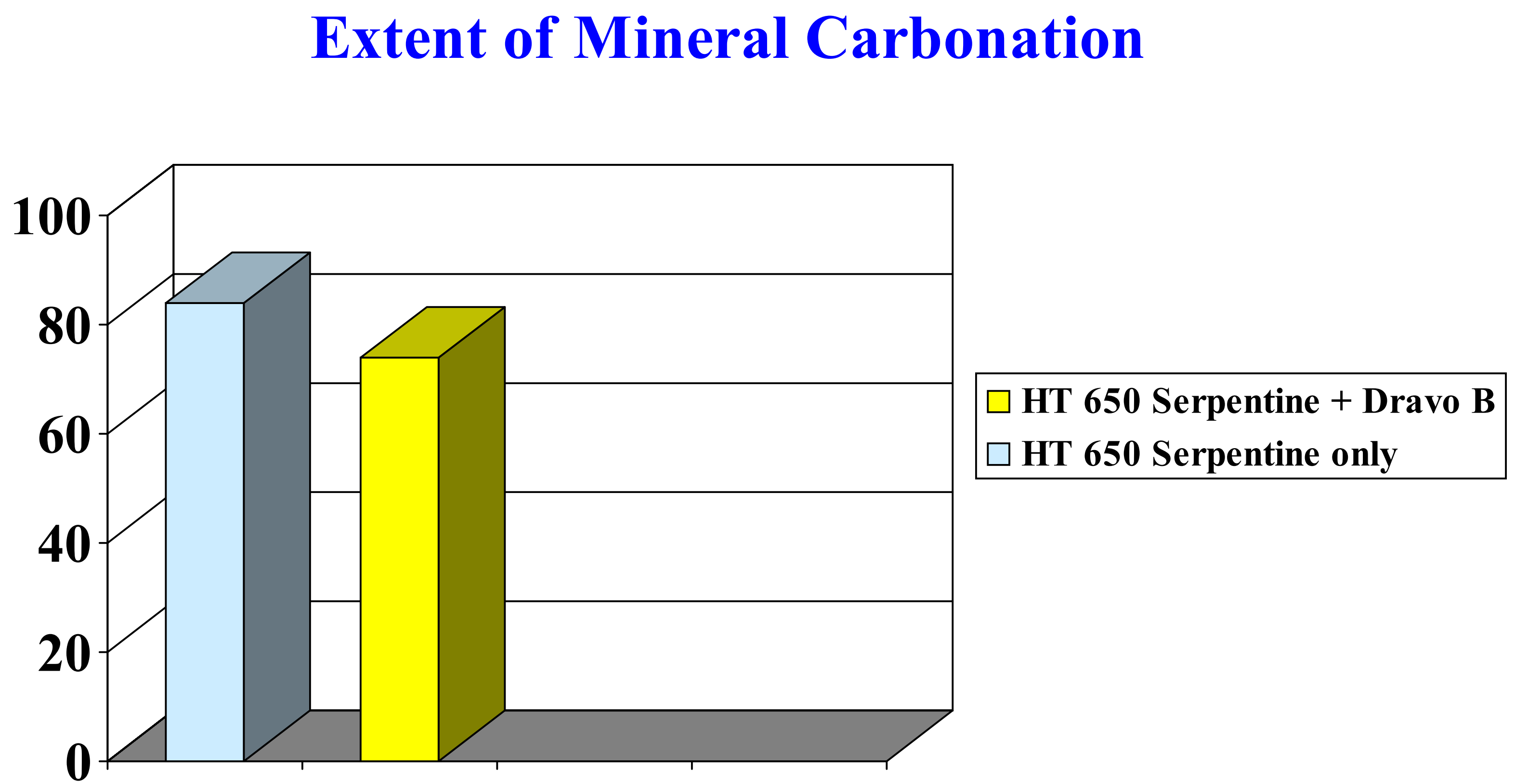
Buffered Solution: 0.5 M Na_2CO_3, 0.5 M $NaHCO_3$, 1.0 M NaCl.
Reaction Time = 30 minutes

Carbonation Efficiency of Olivine
Effect of Dravo B



Olivine, Twin Sisters Range, Washington, USA Bicarbonate Solution: 0.5M Na2CO3; 0.5 NaHCO3; 1 M NaCl , Reaction Time: 30 mins.

HT 650 Serpentine Carbonation Efficiency Effect of Dravo B



Reaction Conditions: T = 155ºC, P_T = 75 atm, Reaction Time = 0.5 hrs. Buffered Solution: 0.5 M Na_2CO_3, 0.5 M $NaHCO_3$, 1.0 M NaCl

NETL Mineral Sequestration Test Summary

- **Continuous-Stirred-Tank-Reactor (CSTR)**
  - Substrate: *Freeman United Coal Mining Fly Ash (High in Mg and Ca) and Consol Energy Spray Dryer Ash*
  - Conditions: P_{total} = 125 atm, Temperature = 185°C
    - Carbonation Solution: 0.5 M Na_2CO_3; 0.5 M $NaHCO_3$; 1.0 M NaCl
    - Carbonation Efficiency: 50% and 72% conversion to carbonates ($CaCO_3$, $CaMg(CO_3)$
  - Observation: By-product conversion to valuable resource for CO_2 sequestration

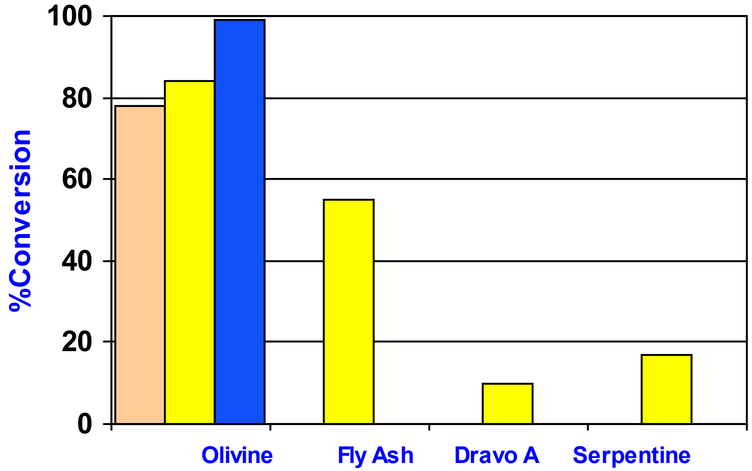
  - Substrate: *Dravo A - Dravo ThioClear® process by-product (High in Ca) and Olivine + Dravo A By-product*
  - Conditions: P_{total} = 75 & 125 atm, Temperature = 155 & 185°C
    - Carbonation Solution: 0.5 M Na_2CO_3; 0.5 M $NaHCO_3$; 1.0 M NaCl
    - Carbonation Efficiency: 10-52% conversion to carbonates ($CaCO_3$)
  - Observation: Significant mineral dissolution. *In-situ* generation of sulfurous acid.

NETL Mineral Sequestration Test Summary

- **Continuous-Stirred-Tank-Reactor (CSTR)**
  - Substrate: Chemically-treated Serpentine (Pennsylvania State University)
  - Conditions: P_{total} = 125 atm, Temperature = 185°C
    - Carbonation Solution: 0.5 M Na_2CO_3; 0.5 M $NaHCO_3$; 1.0 M NaCl
    - Carbonation Efficiency: No conversion observed.
  - Observation: PSU-treated serpentine ~150 m^2/g. (Raw serpentine~15m^2/g) Significant % loss in MgO.

  - Substrate: NaOH-treated Serpentine
  - Conditions: P_{total} = 125 atm, Temperature = 185°C
    - Carbonation Solution: 0.5 M Na_2CO_3; 0.5 M $NaHCO_3$; 1.0 M NaCl
    - Observation: Transformation of raw Serpentine to MgO

Effect of Solution Chemistry & Reactants on the Extent of Mineral Carbonation



Bicarbonate solution: 0.5 M Na_2CO_3; 0.5 M $NaHCO_3$; *X*M NaCl
Temperature = 185°C; Pressure = 115 atms.; Time = 30mins.

Result: Modification of the bicarbonate solution chemistry has substantial impact on the mineral carbonation efficiency.

Summary of Carbonation Experiments

Reactant	HCO_3^- Solution	Pct.Conv., $MgCO_3$
Coal Fly Ash	$Na_2CO_3/NaHCO_3/NaCl$	55
Olivine	$Na_2CO_3/NaHCO_3/NaCl$	84
Dravo A	$Na_2CO_3/NaHCO_3/NaCl$	10
Serpentine	$Na_2CO_3/NaHCO_3/NaCl$	17

Conclusions: Successful conversion of mineral silicates to carbonates at temperatures of 185°C in high pressure aqueous CO_2 solutions, containing NaCl and Na_2CO_3 and $NaHCO_3$.

Coal fly ash identified as valuable resource in mineral CO_2 sequestration.

Future Work

- **Future Work**
  - Chemical and Thermal pretreatment of Serpentine (M.M. Maroto-Valer, The Pennsylvania State University)
  - Characterization of Reaction Products and Geochemical Modeling (Chen Zhu, University of Pittsburgh)

NETL