INVESTIGATIONS OF THE CO₂ SEQUESTRATION REACTION MECHANISMS THAT GOVERN SERPENTINE MINERAL CARBONATION

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Serpentine (Lizardite): Mg₃Si₂O₅(OH)₄

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SEQUESTRATION VIA MINERAL CARBONATION AN INTRIGUING CANDIDATE TECHNOLOGY FOR PERMANENT CO₂ DISPOSAL

• LARGE SCALE: uses Mg-rich minerals (e.g., serpentine and olivine) whose worldwide deposits exceed those needed to carbonate known global coal reserves.

- ENVIRONMENTALLY BENIGN: the carbonation products are already widely present in nature.
- **PERMANENT:** the products (e.g., magnesite and silica) have proven stable over geological time.

THE PRIMARY CHALLENGE

economically viable process development

SEQUESTRATION VIA MINERAL CARBONATION THE POTENTIAL FOR ECONOMIC VIABILITY

AVOIDS LONG TERM STORAGE COSTS

- associated with
 - monitoring,
 - sudden release (e.g., insurance and litigation costs), and
 - sequestration to compensate for leakage to the atmosphere.

• CARBONATION IS EXOTHERMIC:

- in principle no energy is required for carbonation to occur.
- LOW FEEDSTOCK COST:
 - ~\$4-5/ton for mined and milled serpentine.

THE PRIMARY CHALLENGE

To economically accelerate mineral carbonation from a geological to an industrial timescale.

THE CARBON DIOXIDE MINERAL SEQUESTRATION WORKING GROUP

• MANAGED BY FOSSIL ENERGY, WITH MEMBERS FROM THE

- Albany Research Center,
- Arizona State University,
- Los Alamos National Laboratory,
- the National Energy Technology Laboratory
- Penn State University,
- Science Applications International Corporation, and
- the University of Utah.

• PRIMARY GOAL:

To explore the potential for economically viable process development

- accelerating the carbonation process is key:
 - 1) cost-effective feedstock activation
 - 2) new process development

THE AQUEOUS MINERAL CARBONATION PROCESS DEVELOPED BY THE ALBANY RESEARCH CENTER (ARC)



Serpentine Carbonation

 $3MgCO_3 + 2SiO_2 + 2H_2O$

 $Mg_3Si_2O_5(OH)_4 + 3CO_2$

150 °C + 150 atm CO₂

1M NaCl + 0.64 M NaHCO₂

WHERE ARE WE NOW?



Applied ARC research has accelerated mineral carbonation to near completion in < 1 hr.

Heat and mechanical activation are central to enhancing mineral carbonation reactivity.

Although the process is not yet economically viable, it is far from optimized and offers intriguing low-cost process potential

ARIZONA STATE UNIVERSITY

OBJECTIVE: to explore serpentine and olivine feedstock activation and carbonation processes down to the atomic level to identify the key mechanisms that govern carbonation reactivity.

GOAL: to develop the understanding needed to engineer improved materials and processes to enhance carbonation reactivity and lower process cost.

DEVELOPING AN ATOMIC-LEVEL UNDERSTANDING OF THE MECHANISMS THAT GOVERN SERPENTINE HEAT ACTIVATION AND CARBONATION REACTIVITY

• including understanding the structural and compositional characteristics that enhance the carbonation reactivity of heat-activated meta-serpentine.

Serpentine Mineral Structure Types







Lizardite

Antigorite

Chrysotile

Ideal Composition: Mg₃Si₂O₅(OH)₄

THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS (TGA/DTA) INVESTIGATIONS OF THE SERPENTINE HEAT ACTIVATION PROCESS



TGA/DTA analysis illustrated for lizardite

A VARIETY OF META-SERPENTINE MATERIALS ARE QUENCHED WITH KNOWN HYDROXYL COMPOSITIONS DURING TGA/DTA HEAT ACTIVATION SYNTHESIS



The meta-serpentine materials quenched are illustrated for lizardite

X-RAY POWDER DIFFRACTION PROVIDES STRUCTURAL INSIGHT INTO THE REACTIVE META-SERPENTINE MATERIALS THAT FORM*



* XPD patterns shown are for heat-activated lizardite.

MULTIPHASE ANALYSIS OF THE HEAT-ACTIVATED META-SERPENTINE MATERIALS THAT FORM



INFRARED ANALYSIS OF HYDROXYL BEHAVIOR AS A LOCAL STRUCTURE PROBE



CHANGES IN THE LOCAL HYDROXYL ENVIRONMENT INDICATE NEW META-SERPENTINE FORMATION*



* meta-serpentine derived from lizardite with minor chrysotile inclusions

IN SITU INVESTIGATIONS OF THE AQUEOUS SERPENTINE CO₂ MINERAL CARBONATION PROCESS

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- Center for Solid State Science, [#]Science and Engineering of Materials Graduate Program, and ~Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287.
 - A novel microreaction system has been developed to enable *in situ* observations of the mineral carbonation process.

- Synchrotron X-ray diffraction and Raman spectroscopy are used to probe the reaction mechanisms that govern mineral carbonation reactivity.
- The range of meta-serpentine materials that can be generated via heatactivation are being investigated to provide insight into the key features that enhance feedstock carbonation reactivity.
- Advanced computational modeling is integrated to develop an atomic-level understanding of the key materials characteristics and reaction mechanisms that govern carbonation reactivity.



IN SITU X-RAY DIFFRACTION OF MINERAL CARBONATION SHOWS MAGNESITE FORMS DIRECTLY AT 150 °C*



 * Highly disordered meta-serpentine reacted under 150 atm CO₂ at progressively higher temperatures. The patterns from 20 to 125 °C and 150 to 180 °C are collected for 5 and 20 minutes, respectively (intensities renormalized for comparison). The reflections that form are all associated with magnesite.

RAMAN SPECTROSCOPY CONFIRMS DIRECT MAGNESITE FORMATION



META-SERPENTINE CARBONATION REACTIVITY COMPARED WITH X-RAY POWDER DIFFRACTION



* Lizardite with minor chrysotile inclusions

CONCLUSIONS

Serpentine Heat Activation:

- We have successfully isolated a range of heat-activated meta-serpentine materials for several serpentine minerals, including lizardite, antigorite and chrysotile.
- The meta-serpentine materials that form include both α (stage-2) and "amorphous" materials which appear to exhibit a range of disorder.
- IR can identify new "amorphous" phases, complementing XPD and HRTEM analysis.

Mineral Carbonation:

- A novel microreaction system has been developed with controlled T, P, and activity capability to enable *in situ* observations of mineral carbonation (patent pending).
- Magnesite forms without intermediate formation down to 100 °C (150 atm CO₂).
- The disorder associated with meta-serpentine formation appears to be key to enhancing carbonation reactivity.
- Minor amounts of a second serpentine phase in the serpentine feedstock can significantly impact heat-activated meta-serpentine formation and reactivity.

FUTURE WORK

- Complete the meta-serpentine and *in situ* mineral carbonation investigations for the range of materials generated via serpentine heat activation, including those generated from serpentine minerals with select impurities.
- Incorporate new results to enhance the understanding of the key metaserpentine characteristics and mineral carbonation mechanisms that impact carbonation reactivity.

PUBLICATION

• The results described herein have been submitted and are in preparation for submission for peer-reviewed journal publication.