Wellbore Integrity and Mitigation:
Foamed Cement Interactions with CO_2

Presenter: Richard Spaulding

US DOE/ NETL

Verba, C., Montross, S., Spaulding, R., Dalton, L., Crandall, D., Moore, J., Huerta, N., Kutchko, B

U.S. Department of Energy

National Energy Technology Laboratory

Mastering the Subsurface Through Technology Innovation, Partnerships and Collaboration:
Carbon Storage and Oil and Natural Gas Technologies Review Meeting

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Benefit to the Program

- As CO_2 storage options are being evaluated in the United States, the possibility of utilizing offshore formations in the GoM is being considered.
- To mitigate shallow hazards in deepwater Gulf of Mexico, foamed cement systems are recommended by the API 65.
- Previous *in situ* experiments show that the cement, host rock and/or casings result in alteration that may compromise wellbore integrity.

Project Overview:
Goals and Objectives

- Evaluate the geochemical and geomechanical impacts of foamed cement due to interactions with CO_2-saturated brine at subsurface conditions typical in the GoM.
- To provide science and guidance on the risk associated with carbon storage in regions of the GoM where foamed cement use is common.

Technical Status - Methods

Data Sets

1. Generated atmospheric samples using API RP 10 B-4 procedures
   - Class H neat (base density)
   - 3 Foam Qualities (10%, 20%, 30%)

In situ Cure & Exposure

1. 28 day cure at atmospheric conditions
2. Immersed in 0.25 M NaCl brine
3. Exposed to $SCCO_2$ (28.9 MPa, 50°C) for 7, 14, 28, 56 days, 6 months

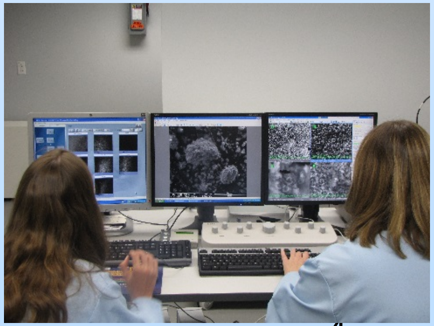
Analysis

Visualization

1. Multi-scale Computed Tomography (CT) Scanning
2. Scanning Electron Microscopy

Mechanical testing

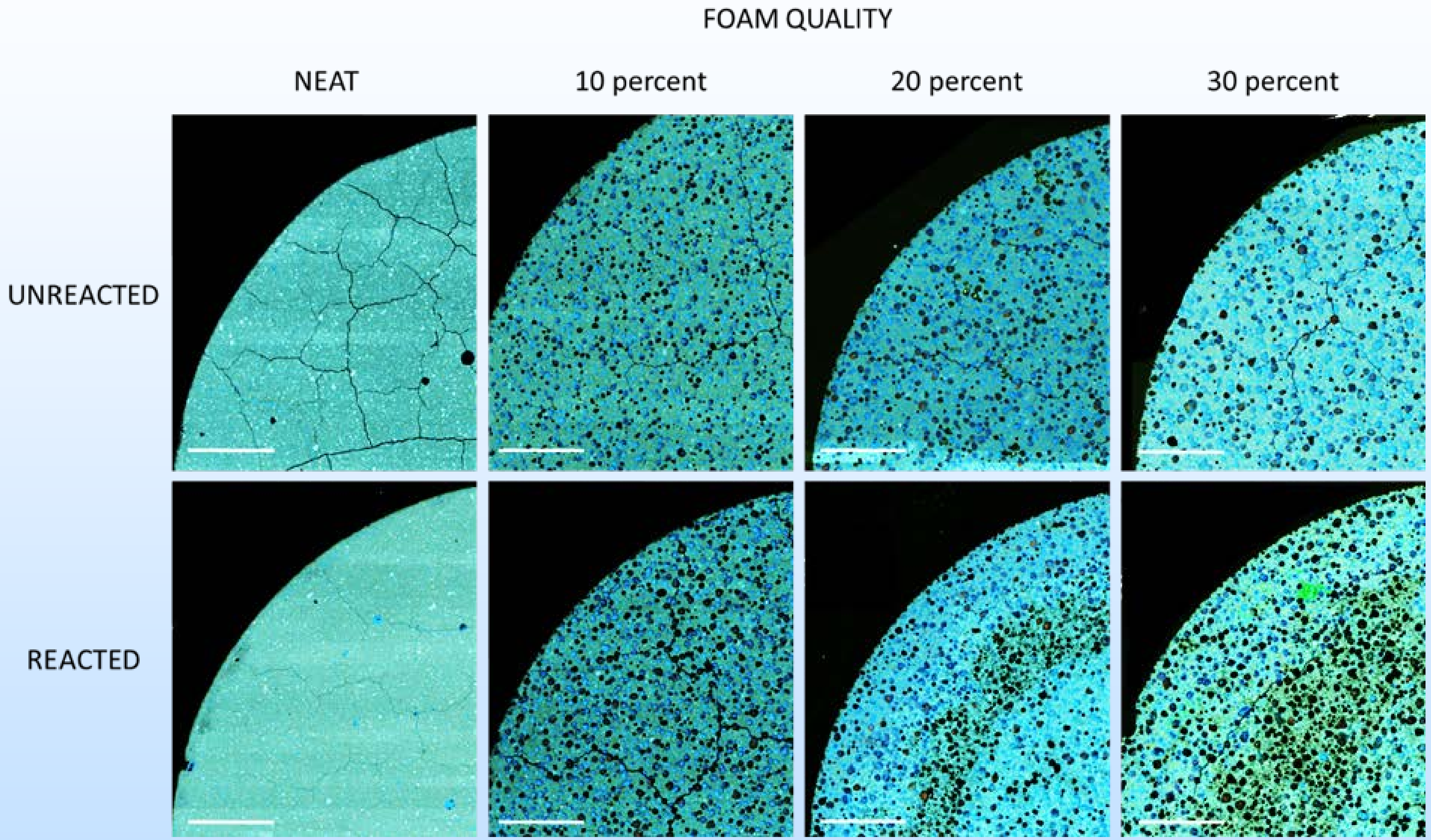
1. Porosity, permeability and strength measurements
   - Young's modulus
   - Poisson's ratio



Geochemical

1. XRD
2. ICP-MS/OES
3. SEM-EDS

Technical Status - Results



SEM backscatter image with of unreacted and reacted (56 days) foamed cement of variable foam qualities (neat, 10%, 20%, and 30%) overlain with elemental maps [Ca- blue, Si green]. Scale bar is 3 mm. Cracks are likely due to sample prep.

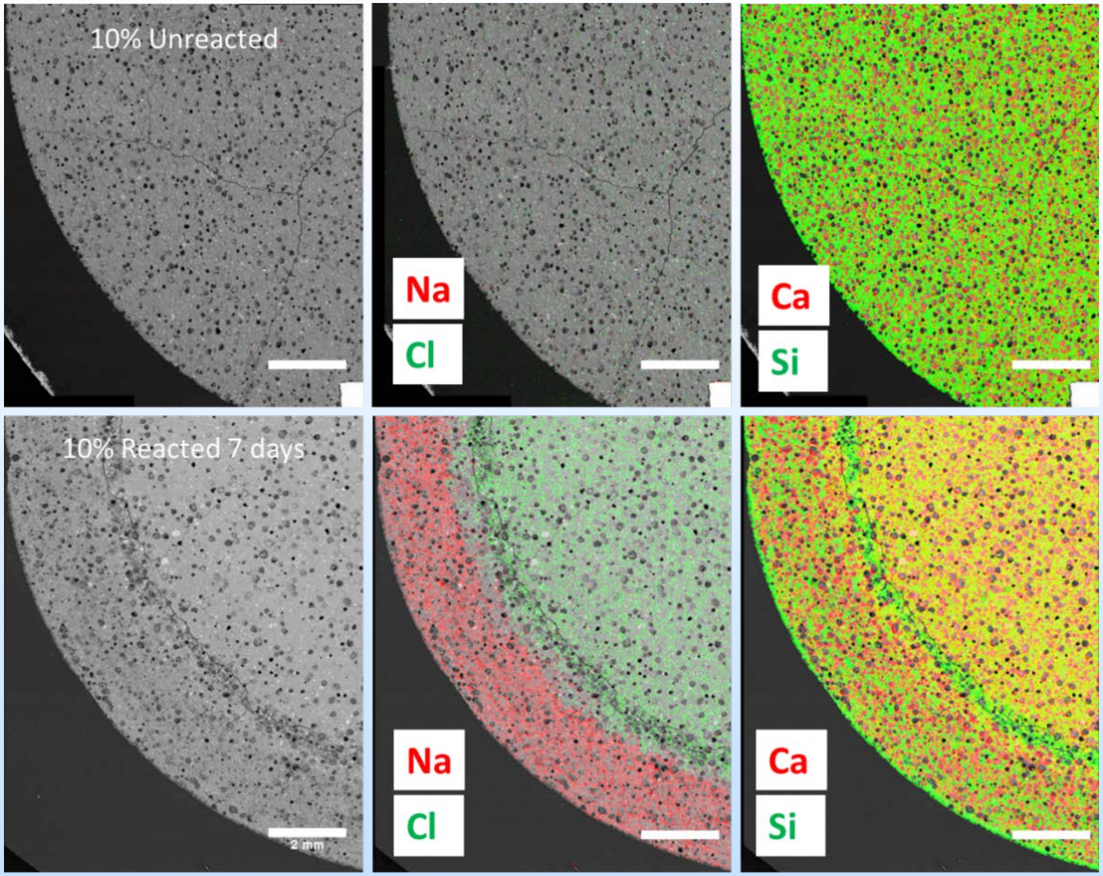
The 30% foam quality cement ~27x alteration as compared to neat cement.

The 20% foam quality ~17x more alteration than neat cement.

The 10% foam quality similar alteration to neat cement.

Total alteration depths in the neat, 10%, 20% and 30% samples were 0.31, 0.10, 5.39, and 8.35 mm respectively.

Technical Status - Results



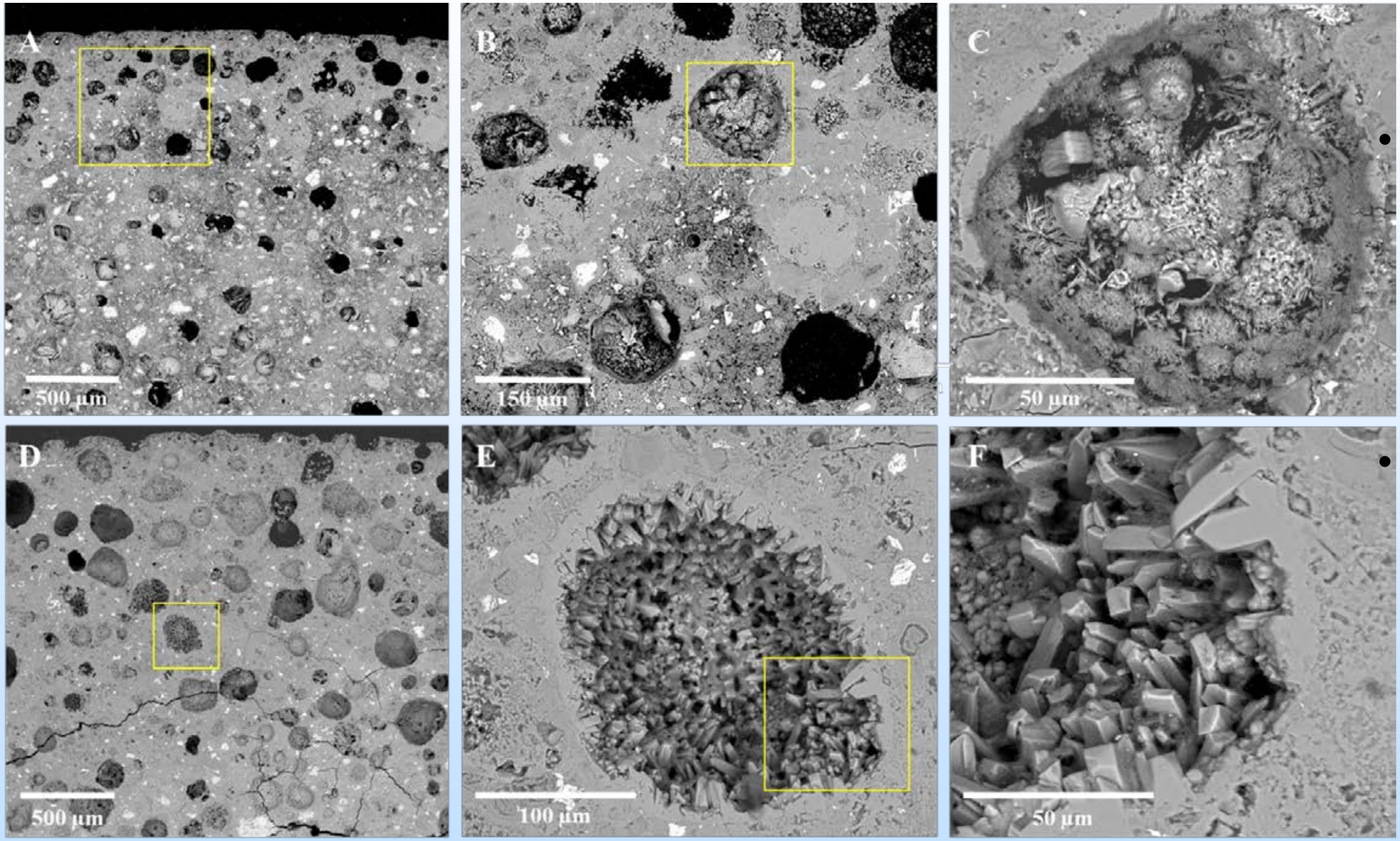
SEM backscattered images of 10% unreacted (top row) and 7-day reacted (bottom row) cement. Center and right images in each row show the distribution of Ca, Na, Si, and Cl in the cement.

The 10% foam quality cement showed evidence for alteration after 7 days

Alteration zone and evidence for redistribution of Ca, Na, Si, and Cl along the outer edge of the cement core

Elemental maps show the detrital outer silica rind as other cations are pulled into solution, a carbonation zone, and a Ca-leached zone

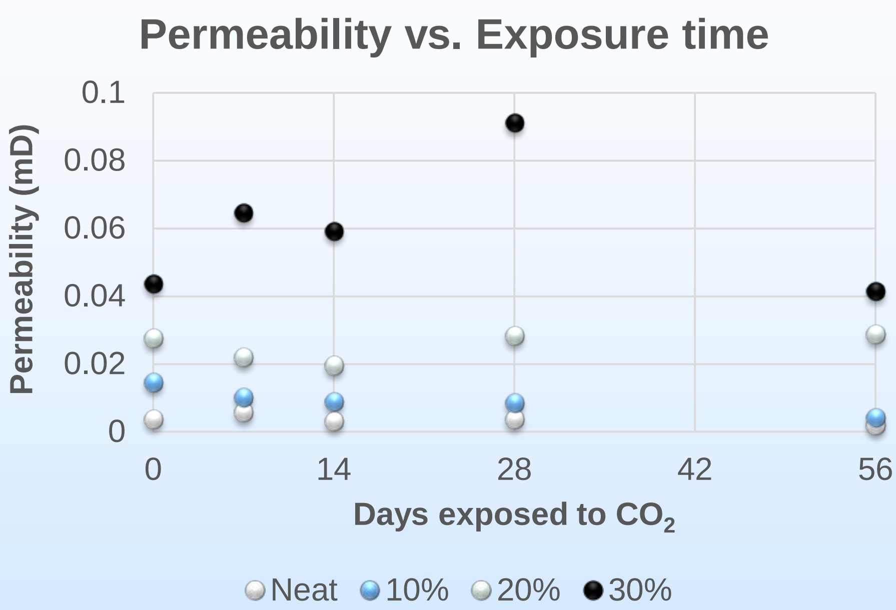
Technical Status - Results

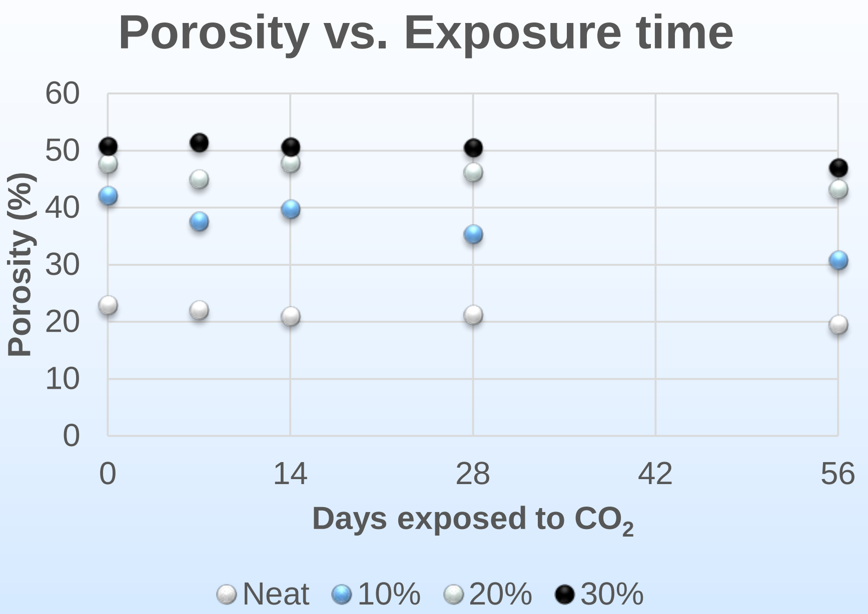


- The bubbles in the alteration zone are filled with calcium carbonate crystals
- Illustrates how carbonation alters pore space by precipitation

SEM backscattered images of reacted (56 days) foam cement samples with 10% (A-C) and 20% (D-F) foam quality examining the changes in pore space.

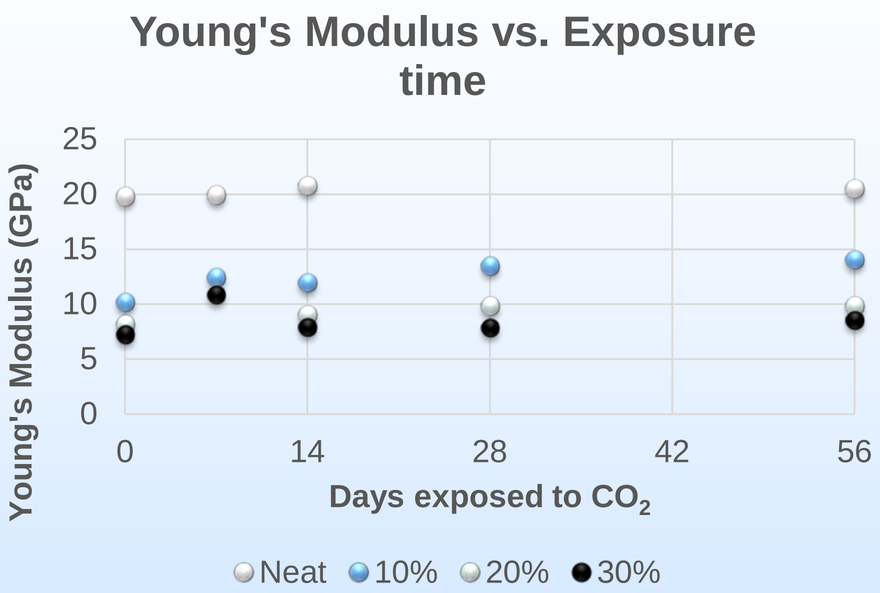
Technical Status - Results

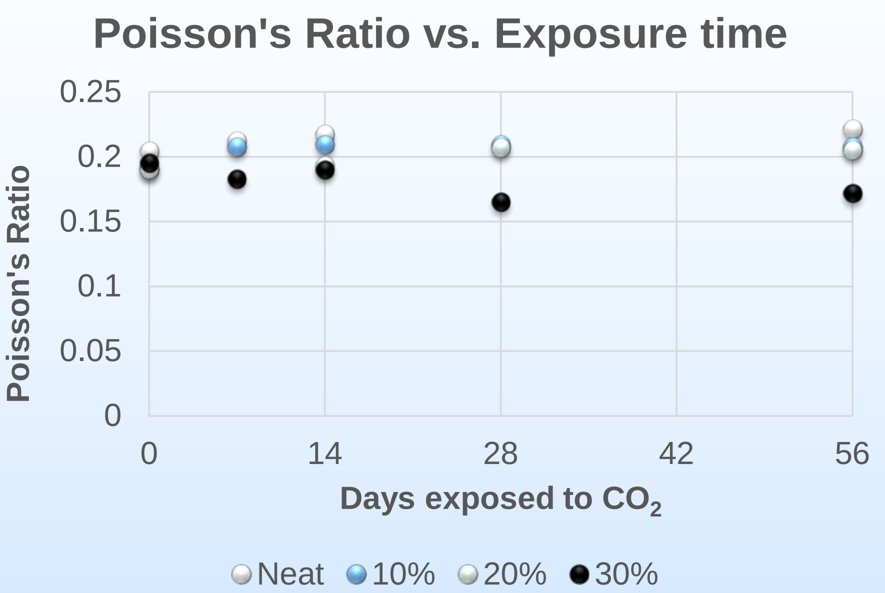




- The permeability of the cement exposed to SC-CO_2 for 56 days decreased by 4.89%, 71.22%, 49.22% for foam qualities of 30%, 10% and neat respectively.
- The permeability of the 20% foam quality sample had an increase of 4.71%. The increase in the 20% or the significant decrease in the 10% will require further study to determine if there are statistical changes.
- The overall trends for porosity show a more stable array of measurements over the entire exposure time. The porosity decreases over the length of the experiment for each foam quality.
- The porosity for the foamed cements decreases by 7.42%, 9.37%, 26.75%, and 15.03% for the 30%, 20%, 10% and neat cement, respectively.

Technical Status - Results

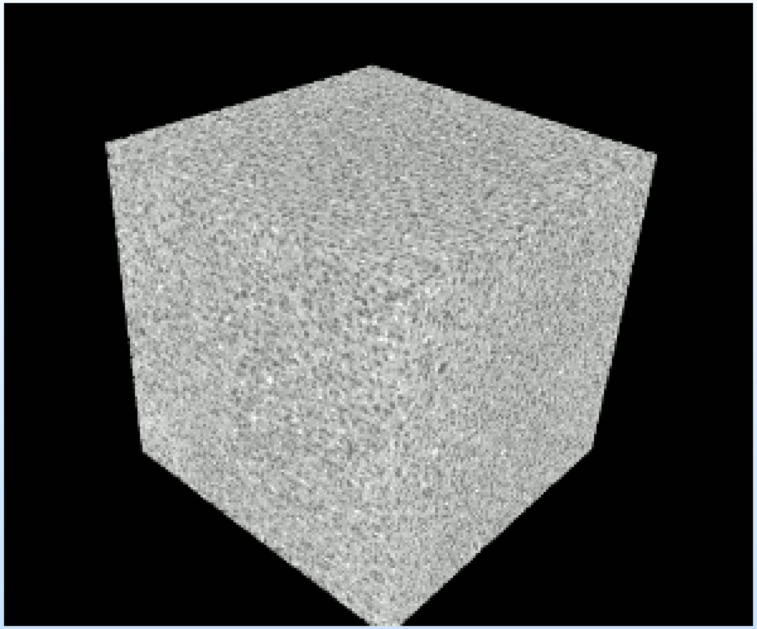




- The mechanical characteristics of these cements show little change in regards to $SCCO_2$ exposure.
- The unreacted cement samples show a decrease in Young's modulus with increasing amounts of entrained air. This is consistent with our previous studies.
- The Young's modulus for all reacted samples over the course of the 56 days of exposure increased. The neat, 10% 20%, and 30% increased roughly 3.48%, 37.95%, 20.29%, and 18.24% respectively. Indicating that long term exposure to $SCCO_2$ can alter the cements ability to withstand deformation.
- All Poisson's ratio values increased over the exposure time except for those associated with the 30% foamed cement.

Project Summary

- The microstructure (bubble size distribution) of the foamed cement has a significant impact on the alteration rate of CO_2
- The CO_2 alteration also has an impact on the microstructure… essentially mineral precipitation in the "bubbles" of the foamed cement.
- Next steps include:
  1. Modeling component to predict the changes in foamed cement properties.
  2. Experimental investigation of $SCCO_2$ saturated brine flow through foamed cement, foamed cement fractures, and along casing-foamed cement microannulus



170,000 individual bubbles identified in 1 cm^3 subsample of a 10% Foam Quality cement

Accomplishments to Date

- **Historical - FY 16**
  - Pre- Post physical properties completed
  - Pre-Post CT scans completed
- **Current - FY 17**
  - SEM-EDS analysis completed
  - CT image analysis completed
  - Mechanical properties near complete (6 month samples)
  - TRS written and published online
  - CCUS 2017 Conference Poster presented
  - Access database for the CO_2 cement mechanical and physical properties is complete and uploaded
- **Future - FY 18**
  - Continued evaluation of the impact of injected CO_2 on the integrity of foamed cement.
  - Correlation of chemical and mechanical alteration

Synergy Opportunities

- Wellbore integrity cross-cuts across all of NETL's portfolios:
  - Offshore
  - Onshore (UNC or otherwise)
  - CO_2 Storage
- Wellbore integrity teams consist of engineers (mechanical, petroleum, environmental), geologists (geophysics, geochemistry), material scientists, fluids specialists, modelers, etc.
- Issues include corrosion (steel components, cement), mechanical, water, cement chemistry, cement mechanics (thermal & pressure cycles), reservoir, etc.
- *Everything we learn from one wellbore integrity project can be applied to the other ongoing projects.*

Thank you

QUESTIONS?

Appendix

– These slides will not be discussed during the presentation, but are mandatory.

Benefit to the Program

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Technical Status - Conclusions

- Foamed cement is significant in that it is commonly used in the Gulf of Mexico and that the microstructure (e.g. BSD) could highly impact the rate of alteration.
- This study shows that foam quality impacts rate of alteration:
  - likely influenced by bubble size distribution.
  - higher foam quality cements displayed a greater degree of alteration as compared to lower foam quality cements.
- Exposure to $SCCO_2$ appears to alter pore geometry:
  - The 30% foam quality cement showed a 25% decrease in pore area after 56 days.
  - The change in pore area is likely result of secondary mineralization (calcium carbonate precipitation).

*It is important to note that all of these results were based on atmospheric-generated foamed cements.

Organization Chart

Project Participants	NETL Teams	Utilized
• Dr. Circe Verba • Dr. Nik Huerta • Dr. Dustin Crandall • Mr. Rick Spaulding • Dr. Scott Montross • Mr. Jim Fazio • Mr. Bryan Tennant • Dr. Barbara Kutchko	Structural Materials Geophysics Materials Characterization Biogeochemistry Geology & Geospatial	• Pittsburgh Geomechanics Laboratory: Chandler Engineering Waring Blenders (cement generating equipment), AutoLab, He-Porosimeter, and N2-Permeameter, various rock saws, and coring equipment • Morgantown CT scanner laboratory, Image processing techniques (high end computers & software needed for image analysis) • Scanning Electron Microscopes, Sample preparation facilities (i.e. polishing wheels and supplies); X-Ray Diffraction facilities • NETL-Albany High Pressure Immersion and Reactive Transport Laboratory • Scanning Electron Microscopes, Sample preparation facilities (i.e. polishing wheels and supplies); X-Ray Diffraction facilities

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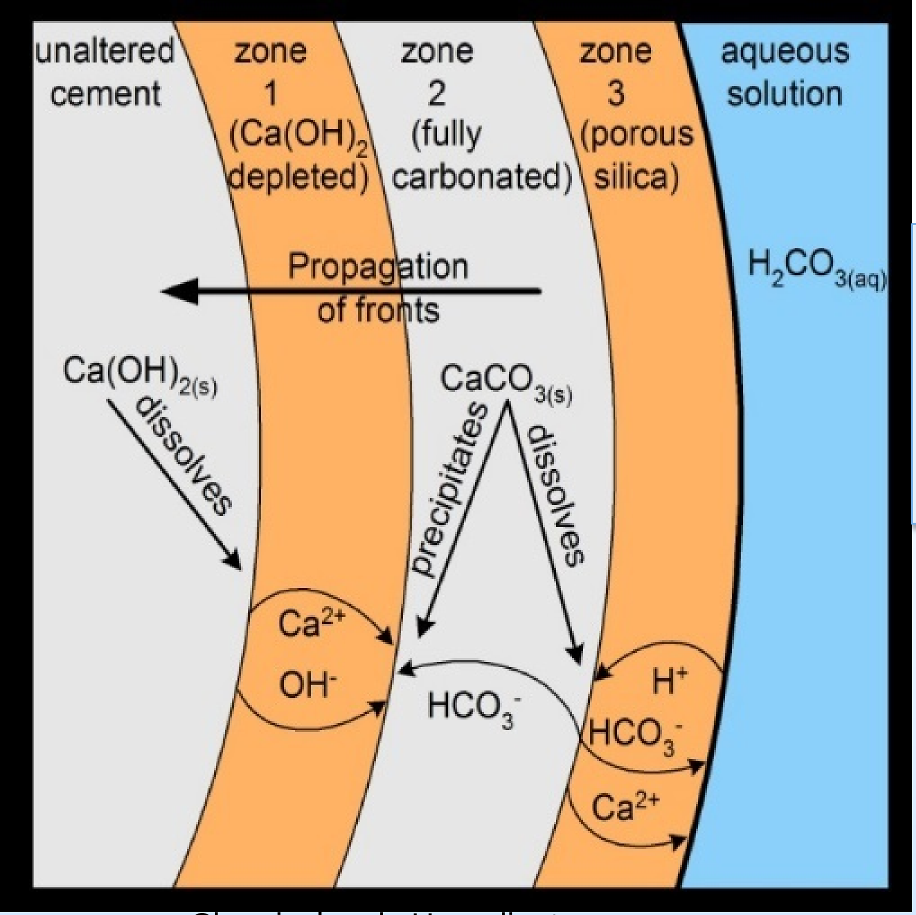

Chemical and pH gradients

- Formation of $CaCO_3$-rich layer (zone 2) creates new, dense phase
- As this phase grows, slower diffusion rates are observed and penetration decreases with time.