Reactive Flow Through Experiments – A Look at Foamed Cement and CO_2 Resistant Cement

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U.S. Department of Energy

National Energy Technology Laboratory

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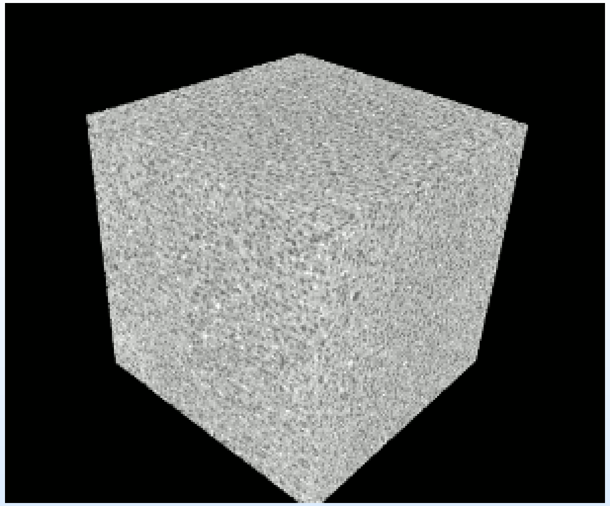
Presentation Outline

- Project Overview
- Background
- Previous Work
- Research Scope
- Results
- Future Work

Project Overview: Goals and Objectives



Goal

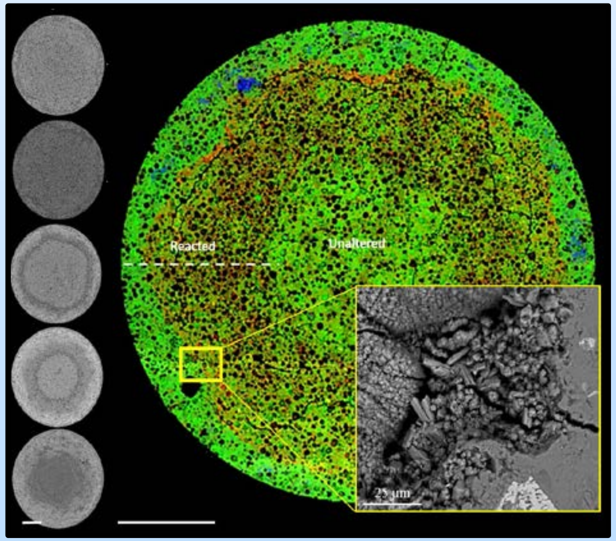
- The objective of the effort is to investigate and evaluate the fracture opening or self-sealing of foamed cements and CO_2 resistant cements: Flow-through CO_2-saturated brine interactions at subsurface conditions typical in the Gulf of Mexico (GOM).

Research Questions

- Will foamed cements with a leak pathway (i.e. fracture) self-seal in a similar manner as ordinary Portland cement?
- When are CO_2-resistant cements needed?
  - Significantly more expensive to use than traditional Portland cements. In addition, they create problems for service companies because they are not compatible with the traditional Portland cements used in other sections of the well.
- When can we use Portland cements and when should we use a specialized cement?
- These answers will improve safety, well integrity, and have significant economic benefits.

Approach

- It is unfeasible to run experiments on every single variable that exists in the subsurface. Therefore, the team needs to understand the fundamental mechanisms to make predictions. Flow-through experiments are being conducted on various cement formulations.



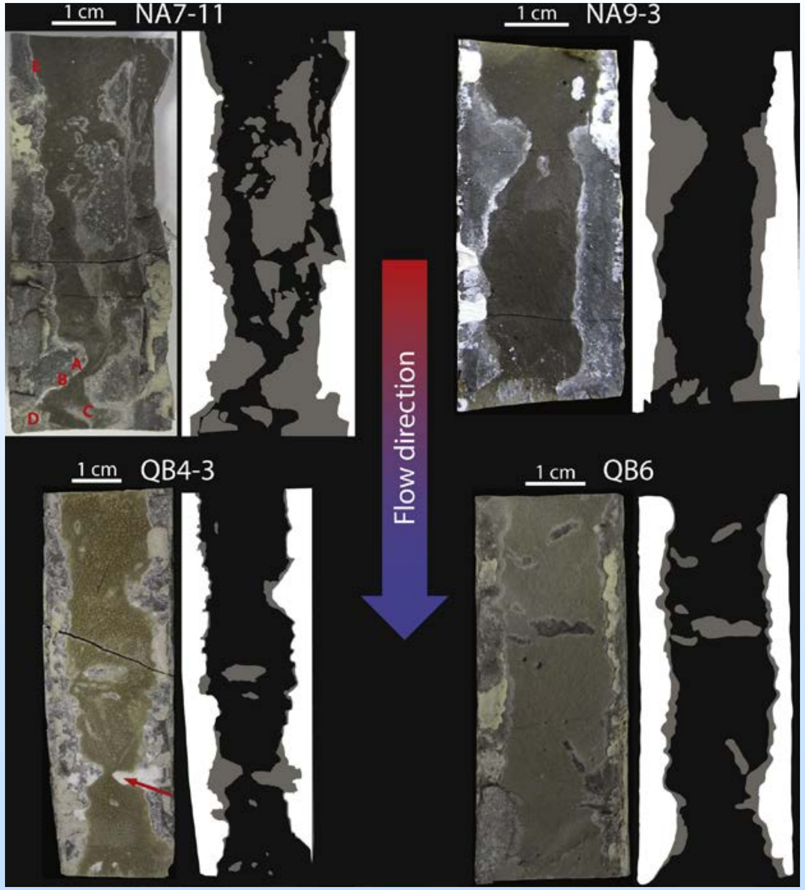
This project is in it's second year

Background

Previous studies have shown that the self-healing ability of cement is likely a combination of several factors:

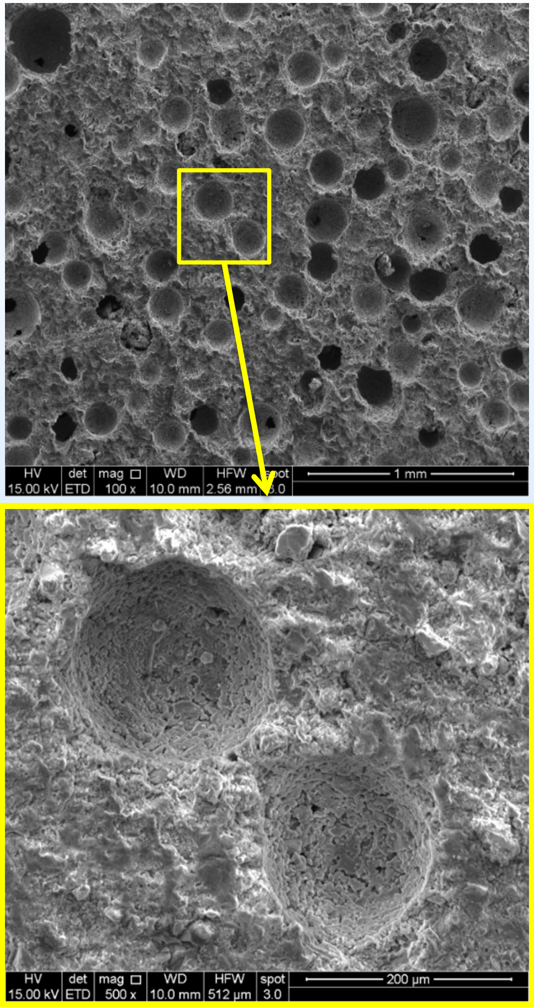
- fracture geometry (aperture size and domain length)
- cement type
- time
- fluid flow rate
- fluid composition
- reservoir conditions

Research has shown that Ordinary Portland Cement (OPC) can self-heal under a wide range of conditions.

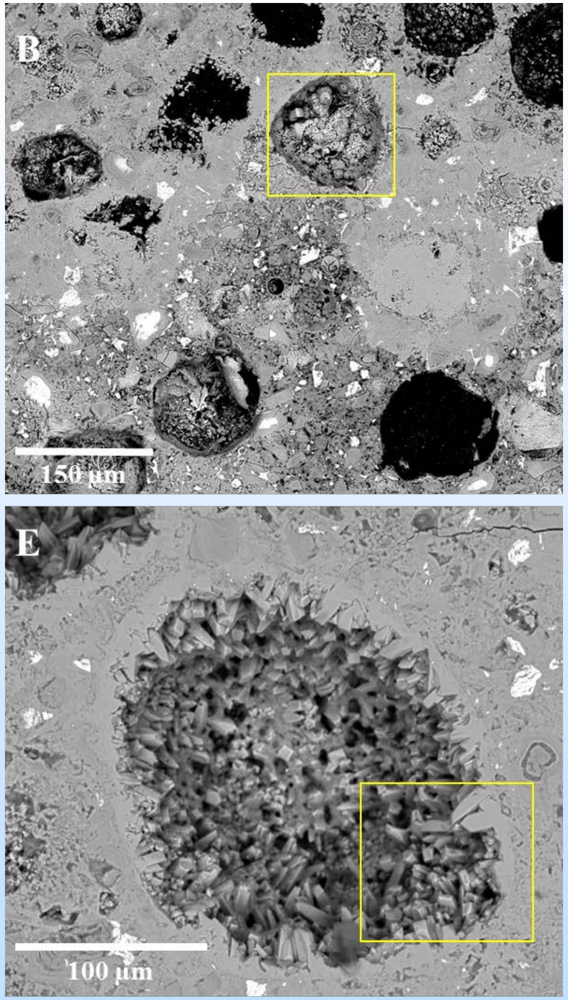


Huerta et al, 2013, 2015

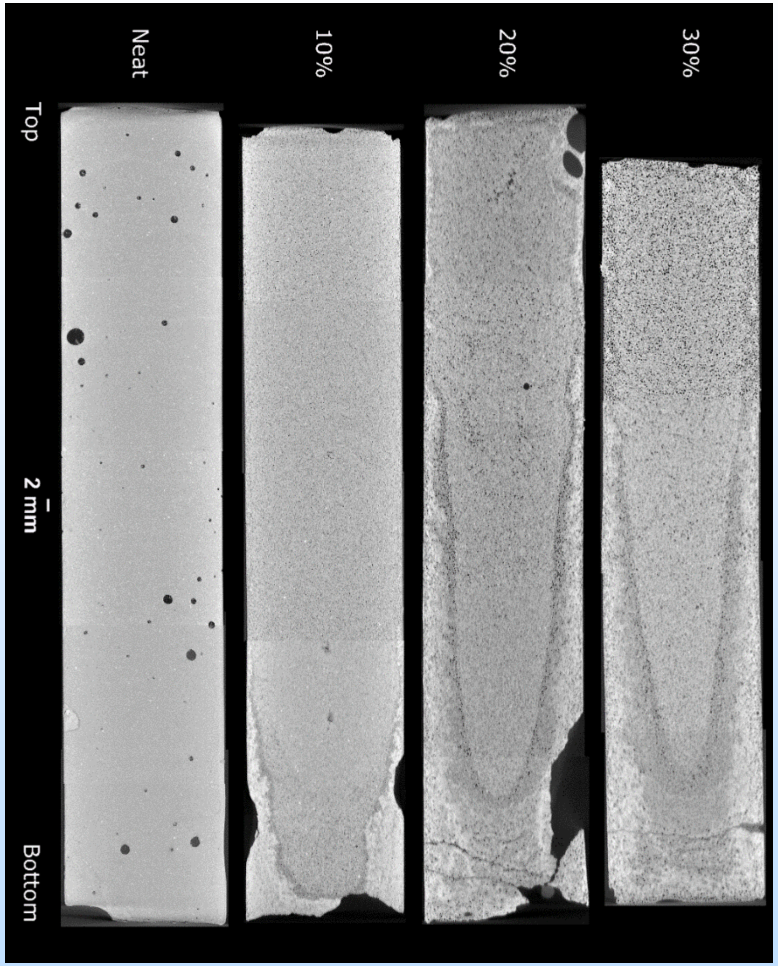
Previous Research



Unexposed foamed cement



Foamed cement exposed to $SCCO_2$ under static conditions (56 days)



Stitched CT Core montage on the XZ direction for neat, 10%, 20% and 30% cores exposed for 6 months. Stitched from approximately 9,000 2D images associated with the full scan of the core

The bubbles in the alteration zone are filled with calcium carbonate crystals

Illustrates how carbonation alters pore space by precipitation

Current Research Scope

Samples

1. Generate foamed cement using API RP 10 B-4 procedures
   a. Three different foam qualities (10%, 20%, and 30% gas volume)
2. Generate various CO_2-resistant cements
   a. Fly Ash-modified Calcium Aluminate Phosphate Cements (Na_2O-CaO- Al_2O_3-SiO_2-P_2O_5-H_2O system)

Experiments

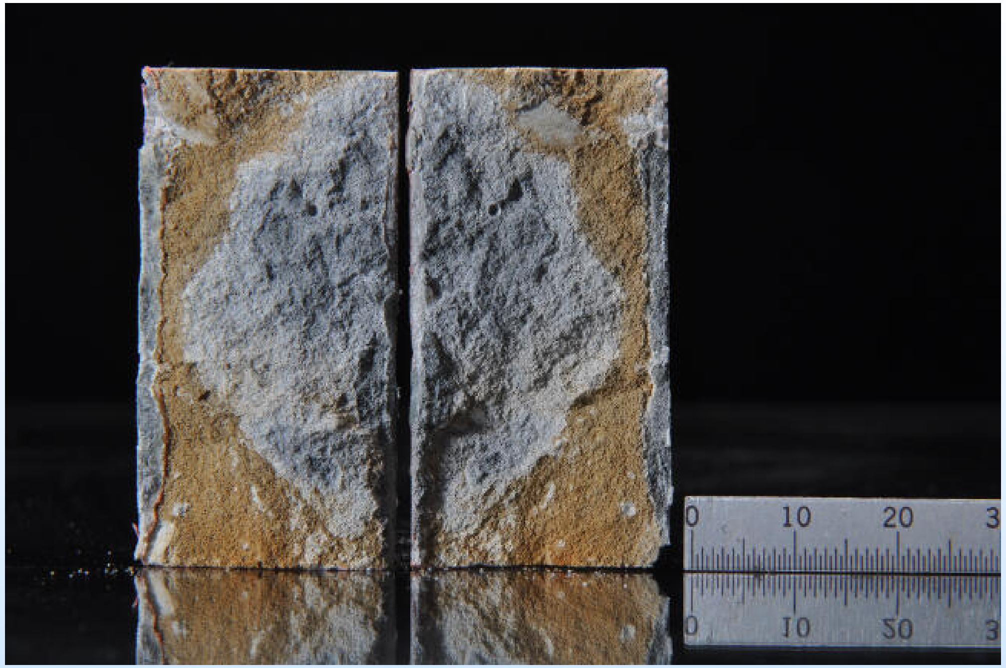
1. Cement cores fractured using the Brazilian method
2. Uniaxial Hasler cells with a confining pressure to create flow through the cement core
   a. Predetermined flow rates for predetermined lengths of time.
   b. In consideration are variable flow and constant flow rates.
   c. Constant flow rate short core experiments
   d. Constant pressure differential composite core experiments
3. CT- flow-through experiments

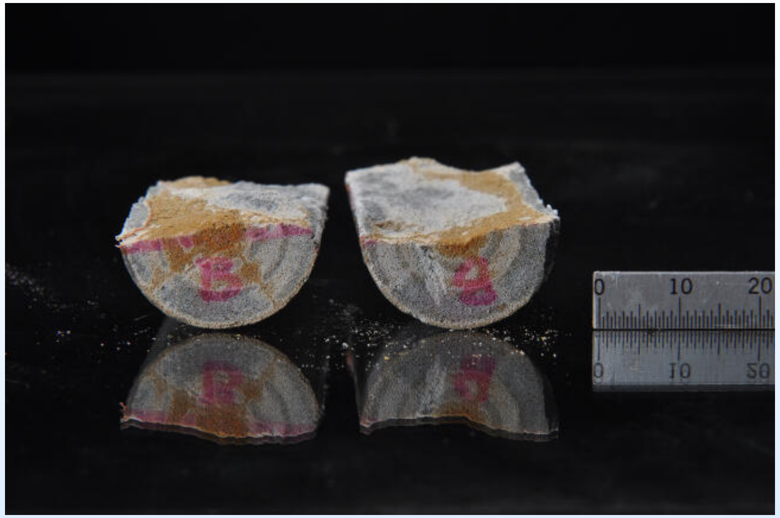
Analysis

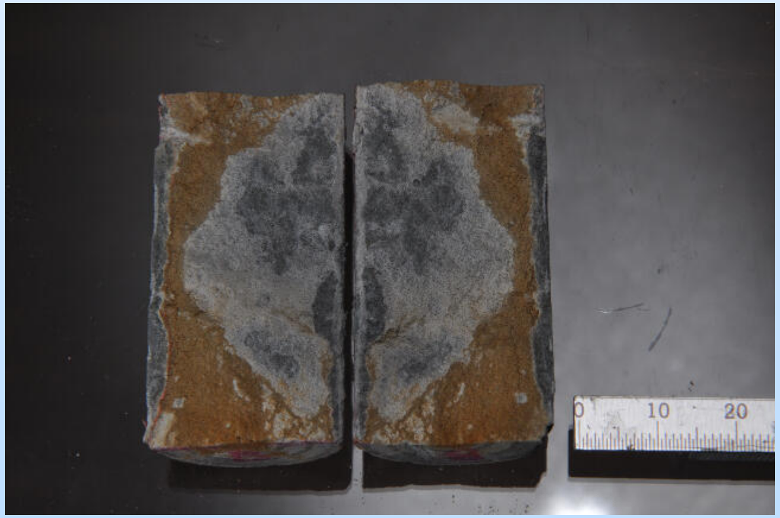
1. Multi-scale computed tomography (CT) scanning*
2. Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS)
3. ATR-FT-IR (Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy
4. Mechanical testing
   a. Porosity
   b. Permeability
   c. Strength measurements

RESULTS

Ordinary Portland Cement

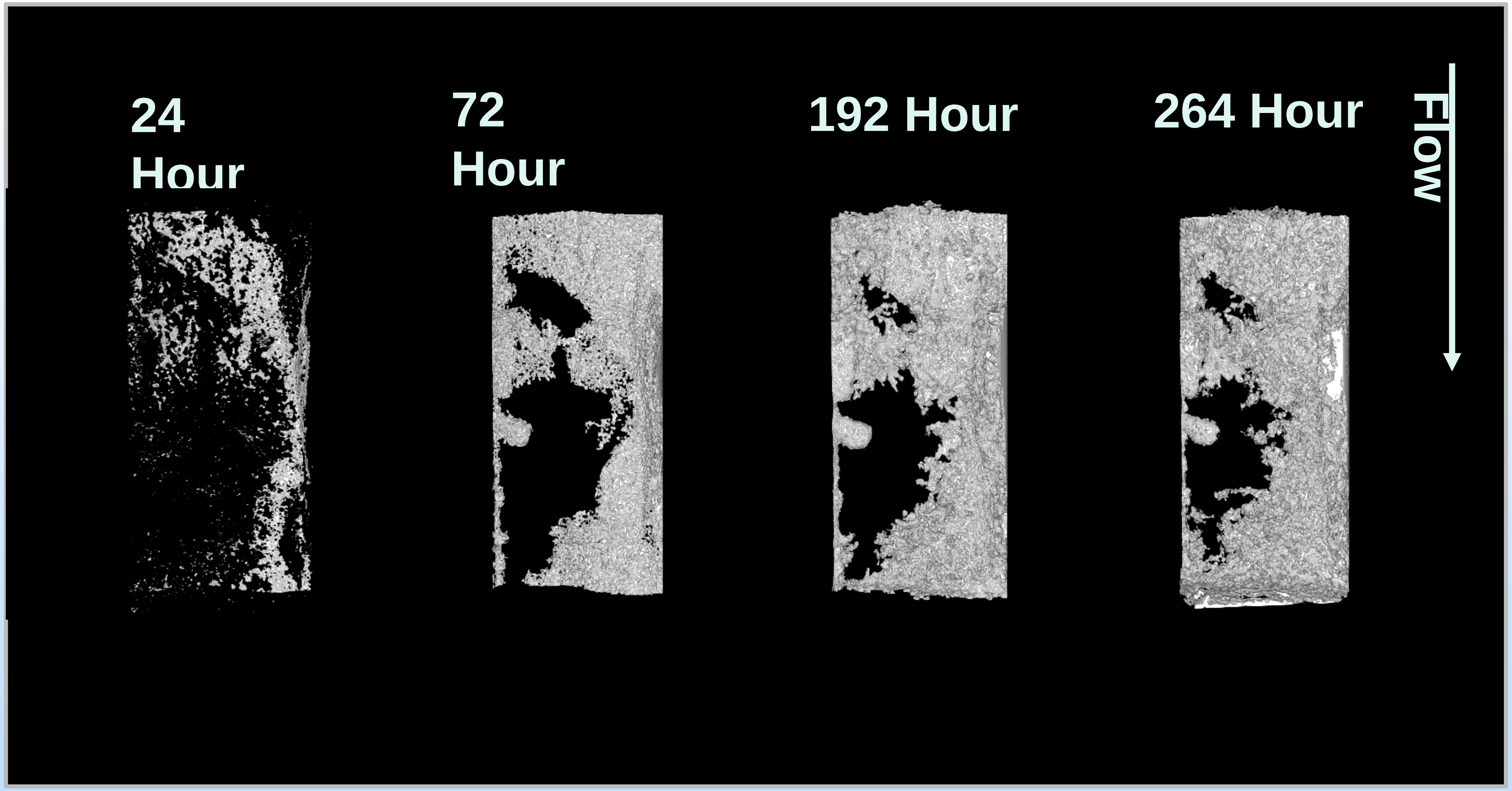




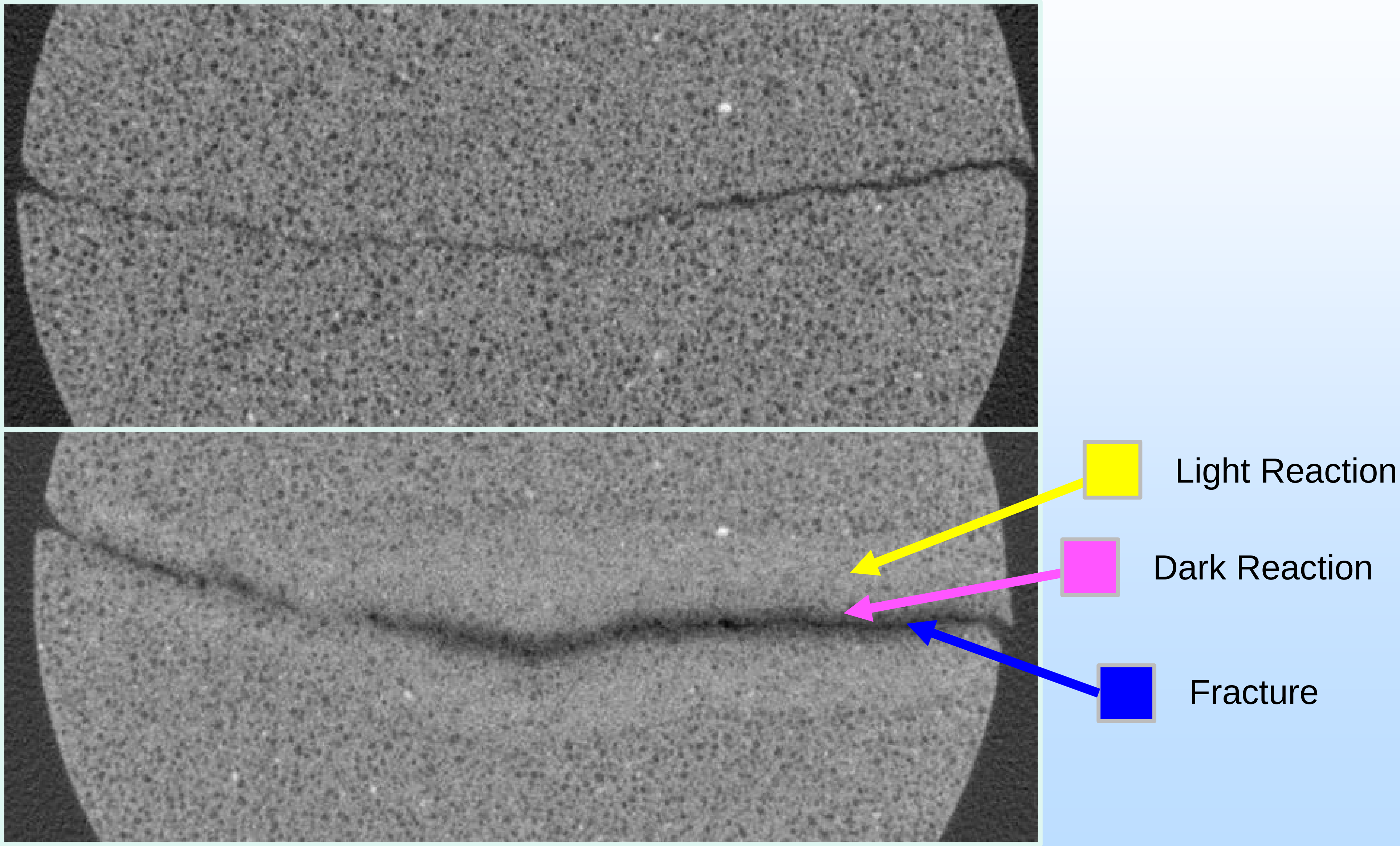


Photos of foamed cement sample (20% foam quality) exposed to variable flow of saturated CO_2 in the medical CT scanner

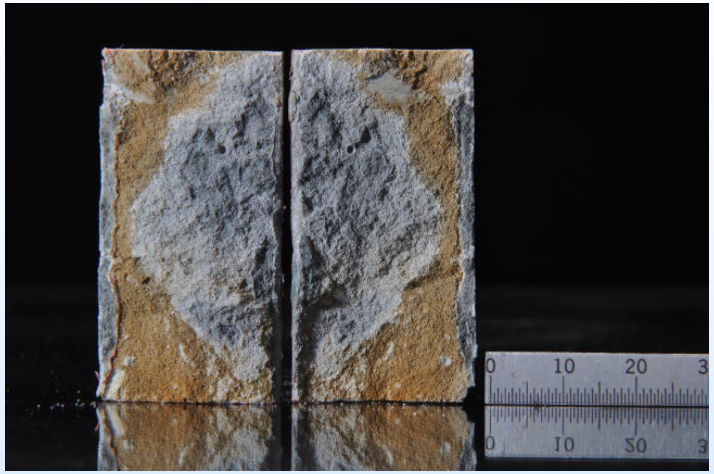
CT-Scanner - Reaction Zone Development



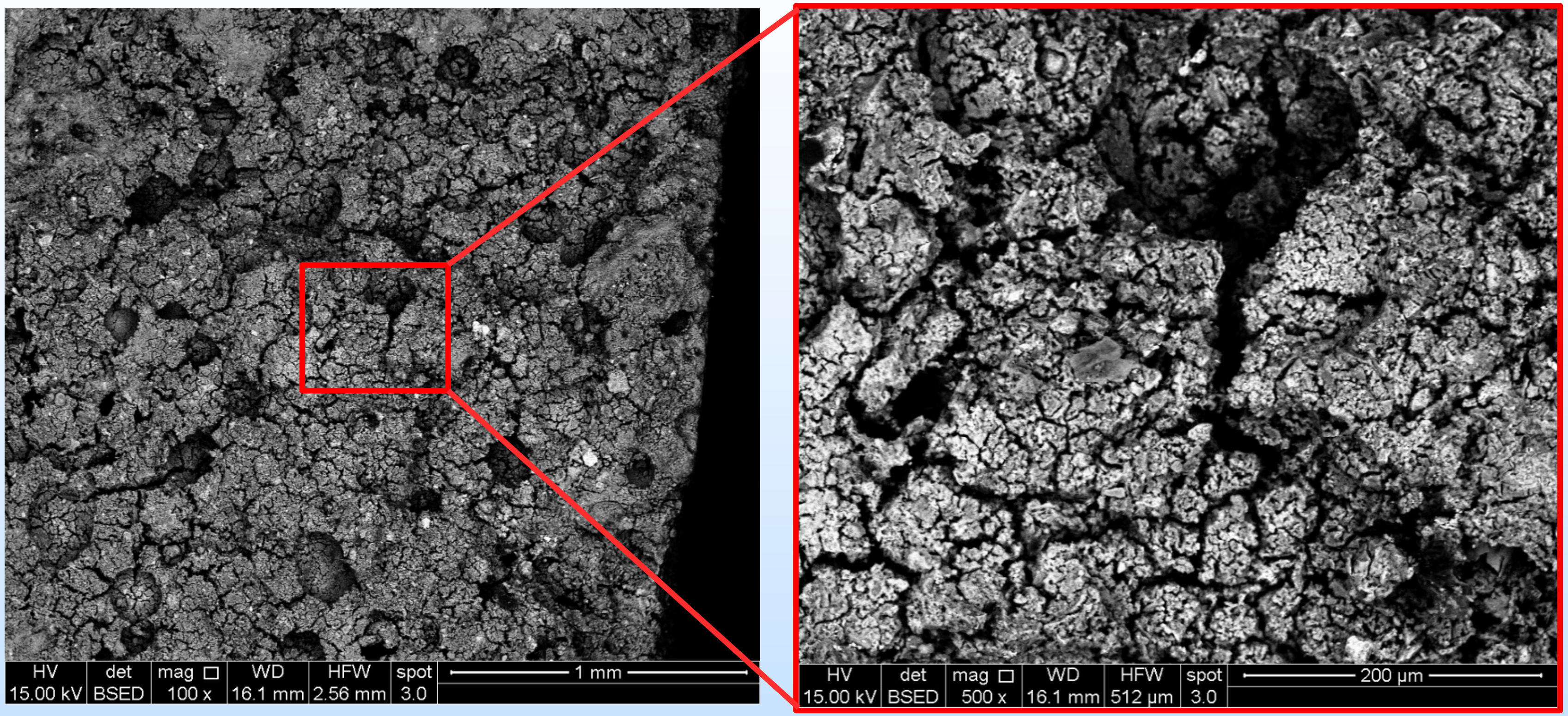
CT-Scanner - Reaction Zone Development



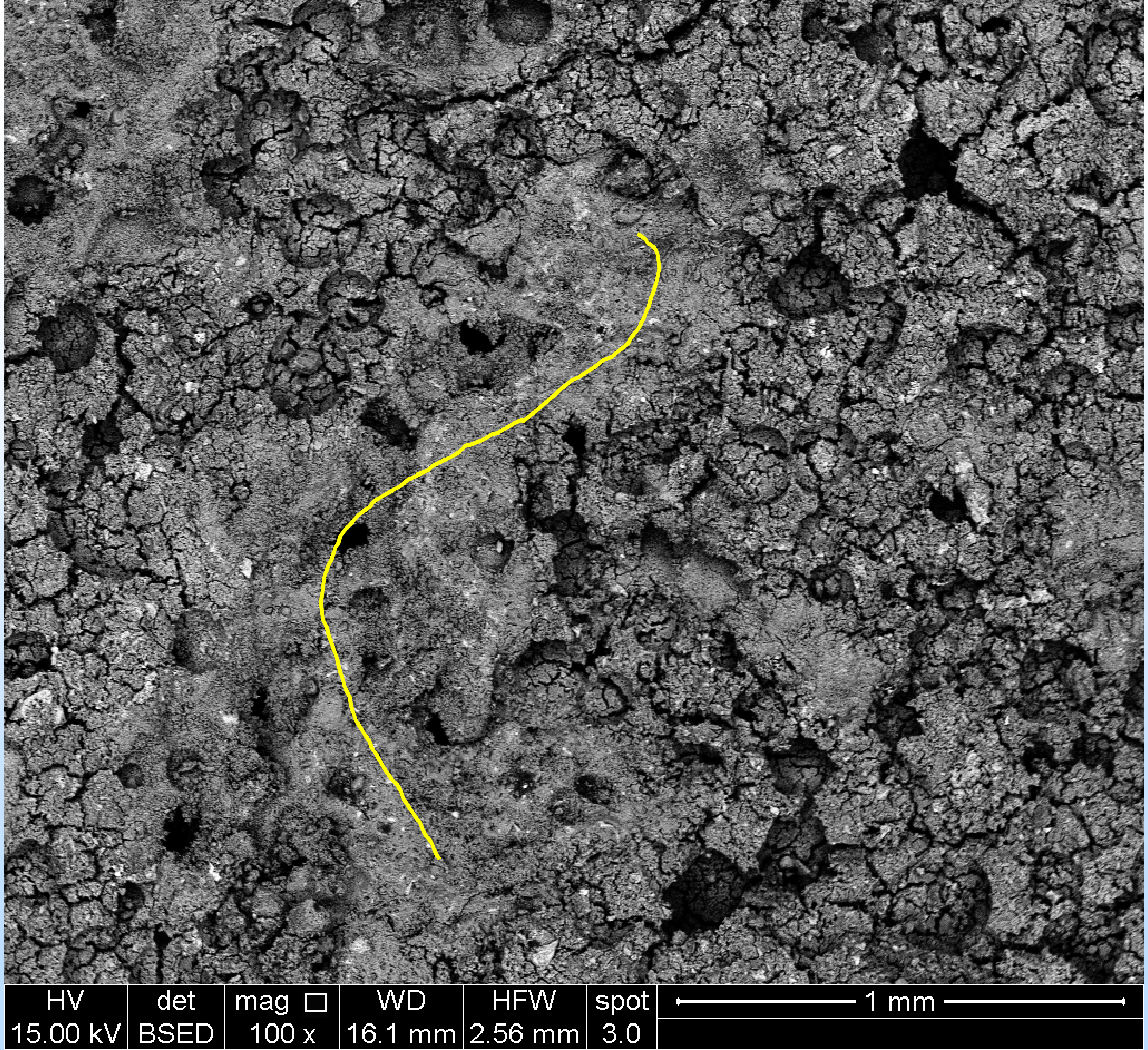
Scanning Electron Microscope

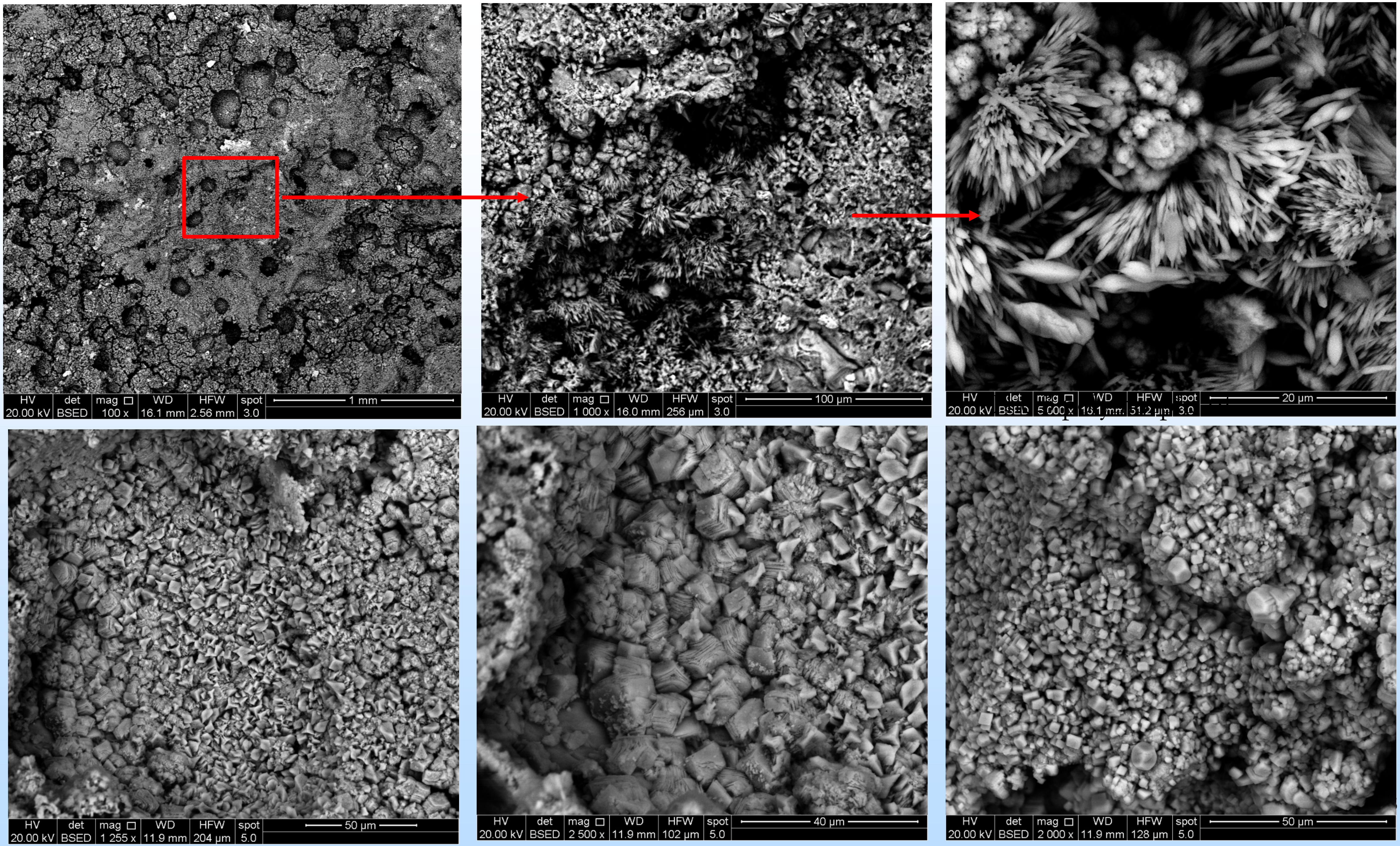


SEM image of a 20% foam quality foamed cement sample that was exposed to variable flow of saturated CO_2 in the medical CT scanner.



Inlet and moving towards the interior


HV
15.00 kV
det
BSED
mag
100 x
WD
16.1 mm
HFW
2.56 mm
spot
3.0
1 mm


HV 20.00 kV det BSED mag 100 x WD 16.1 mm HFW 2.56 mm spot 3.0
1 mm
HV 20.00 kV det BSED mag 1 000 x WD 16.0 mm HFW 256 µm spot 3.0
100 µm
HV 20.00 kV det BSED mag 5 000 x WD 16.1 mm HFW 51.2 µm spot 3.0
20 µm
HV 20.00 kV det BSED mag 1 255 x WD 11.9 mm HFW 204 µm spot 5.0
50 µm
HV 20.00 kV det BSED mag 2 500 x WD 11.9 mm HFW 102 µm spot 5.0
40 µm
HV 20.00 kV det BSED mag 2 000 x WD 11.9 mm HFW 128 µm spot 5.0
50 µm

OPC samples analyzed to establish a proper methodology

Flow direction

Sample A4

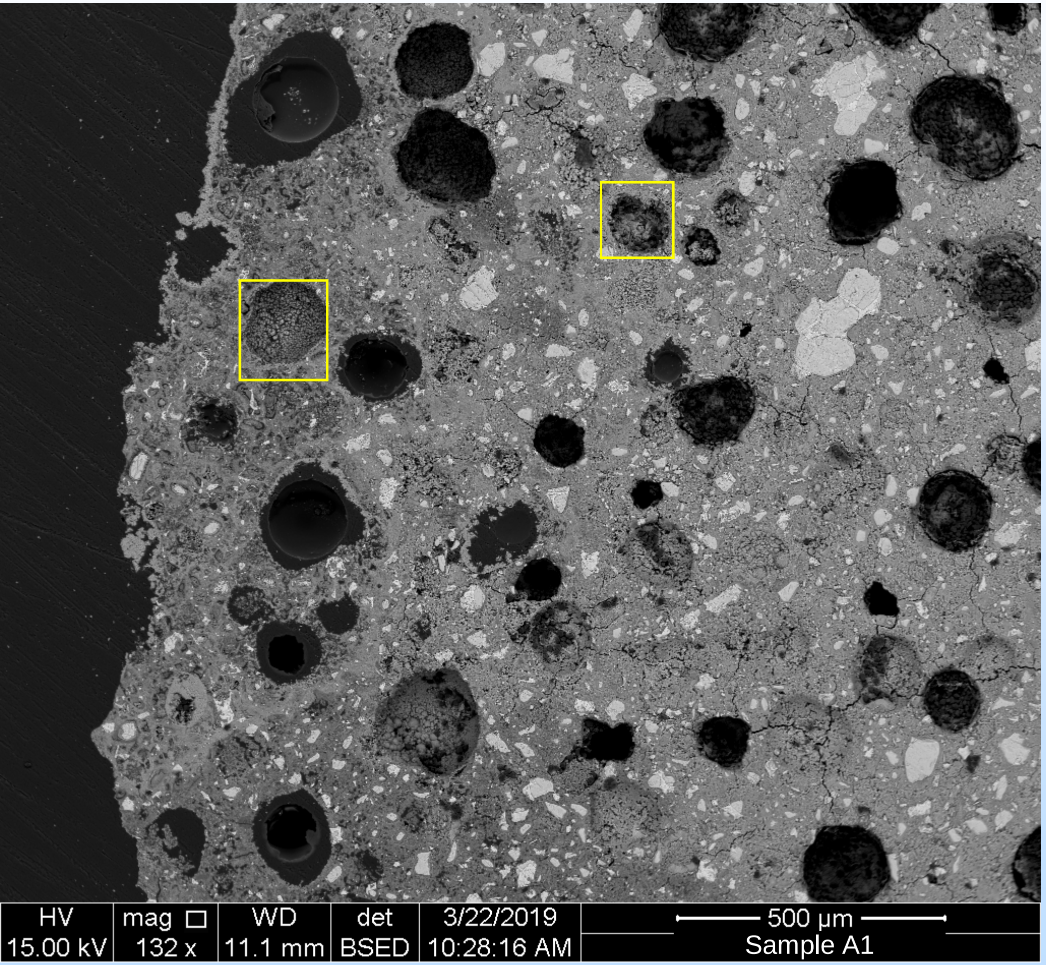
5.6cm,
0.03-0.2mL/min,
60mL fluid flowed,
0.18md to 0.03md

Most reaction happens within 5cm
Flow is channelized

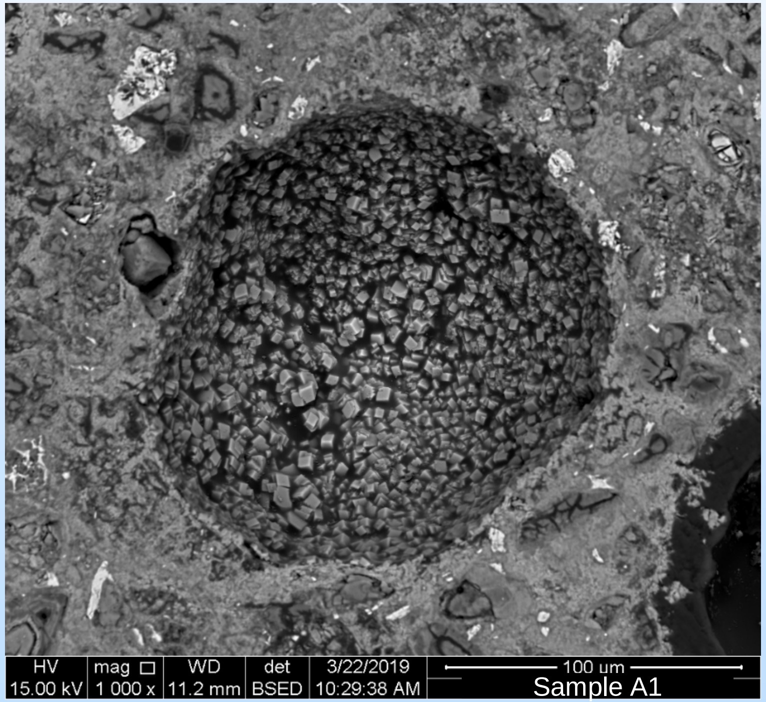
Sample A1 Sample A3

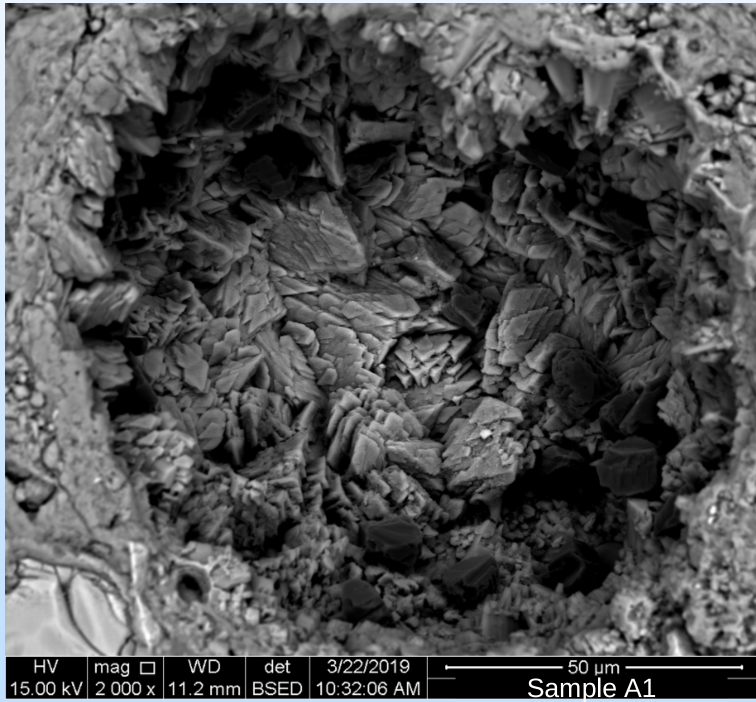
10.3cm,
0.05mL/min,
50mL fluid flowed,
0.17md to 0.10md

OPC cross section, Sample A1

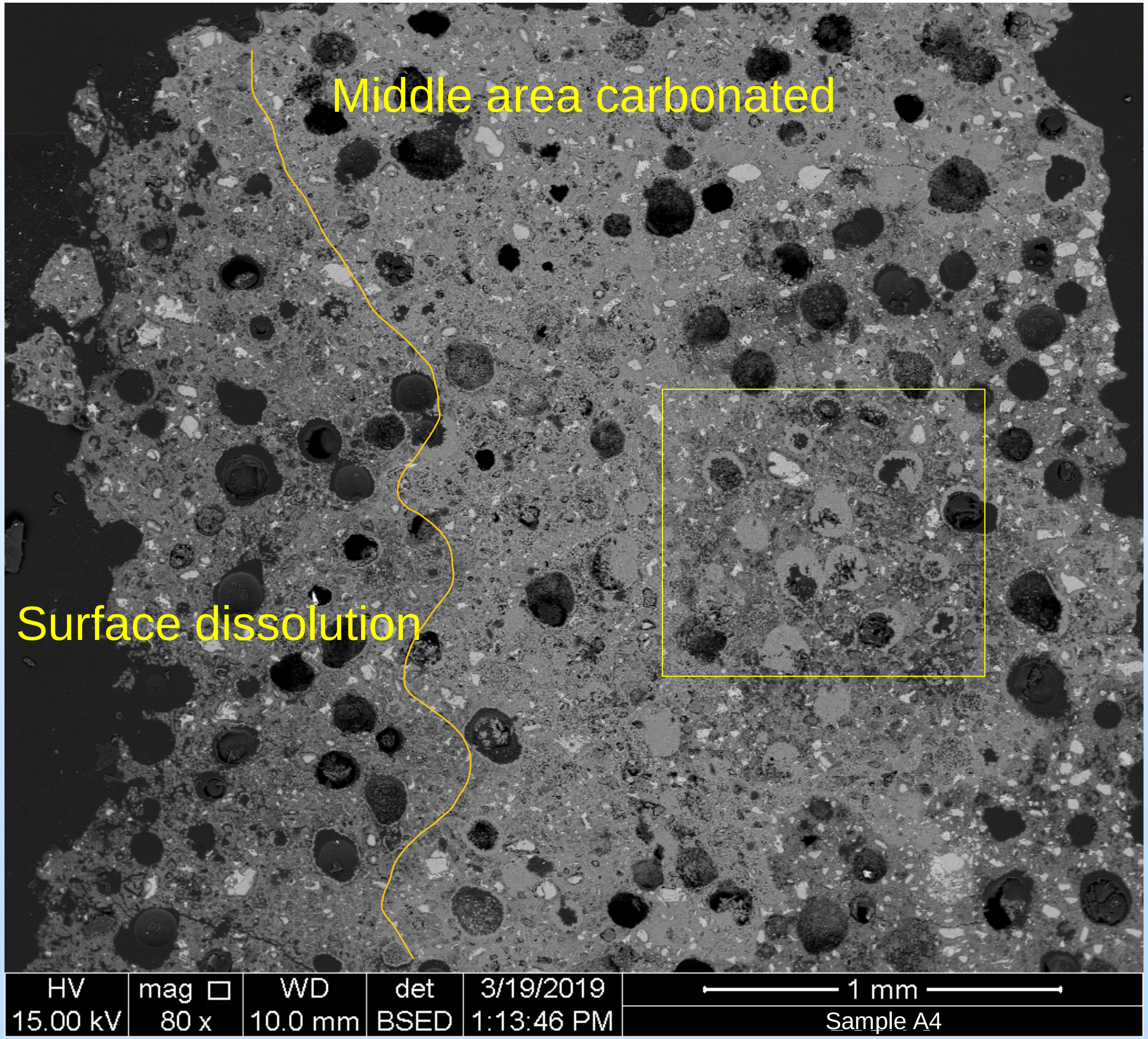


1 mm at 3 cm

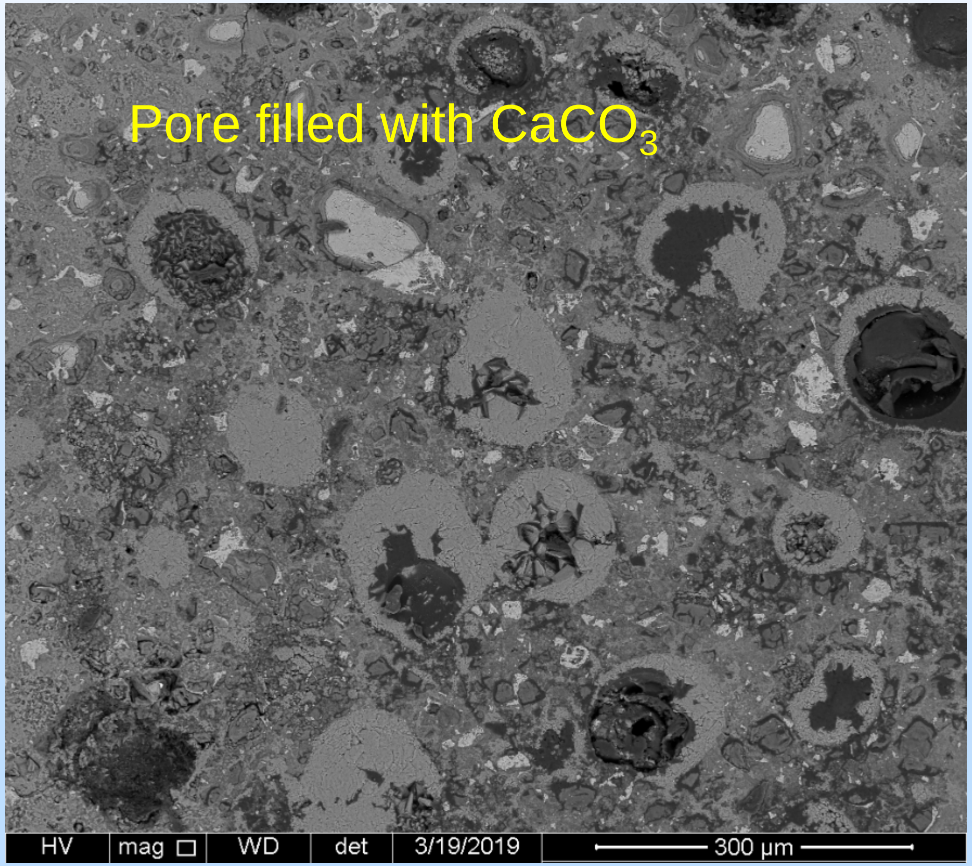




OPC cross section, Sample A4



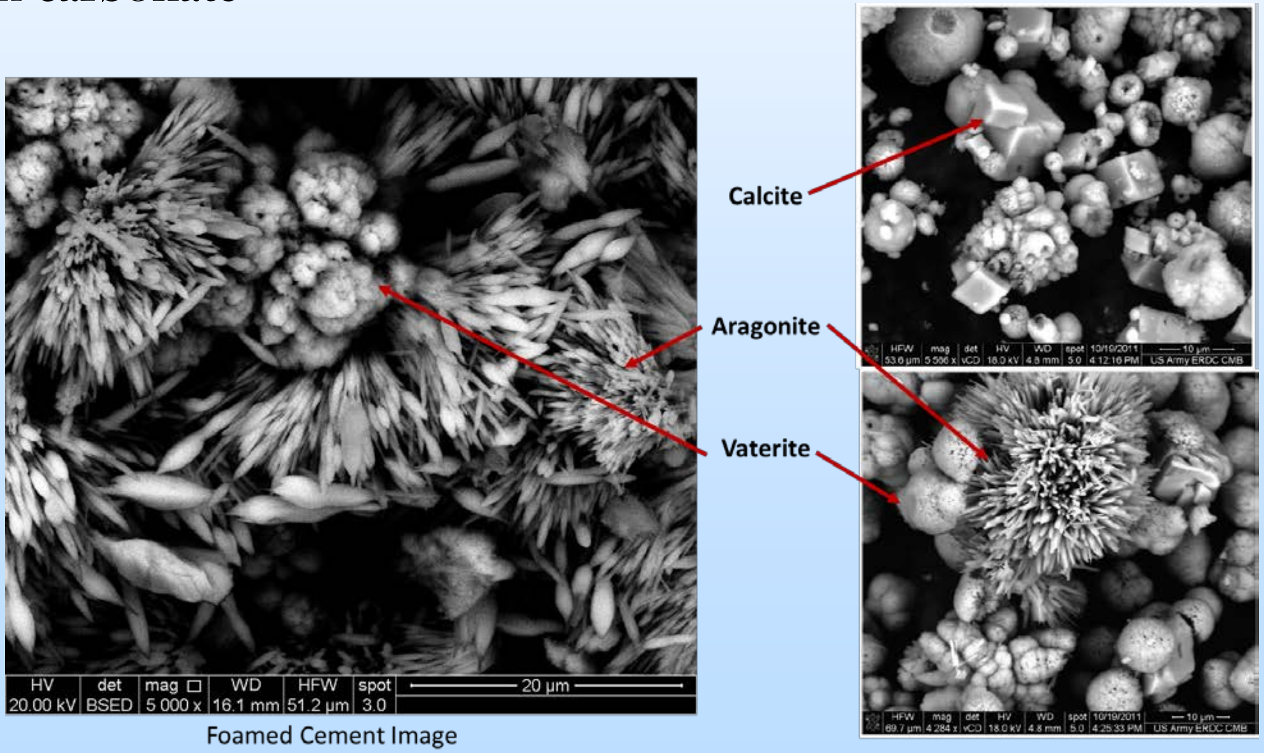
3mm at inlet



Fourier Transform Infrared Spectroscopy

– IR spectroscopy was used to further investigate the SEM analysis that showed that:

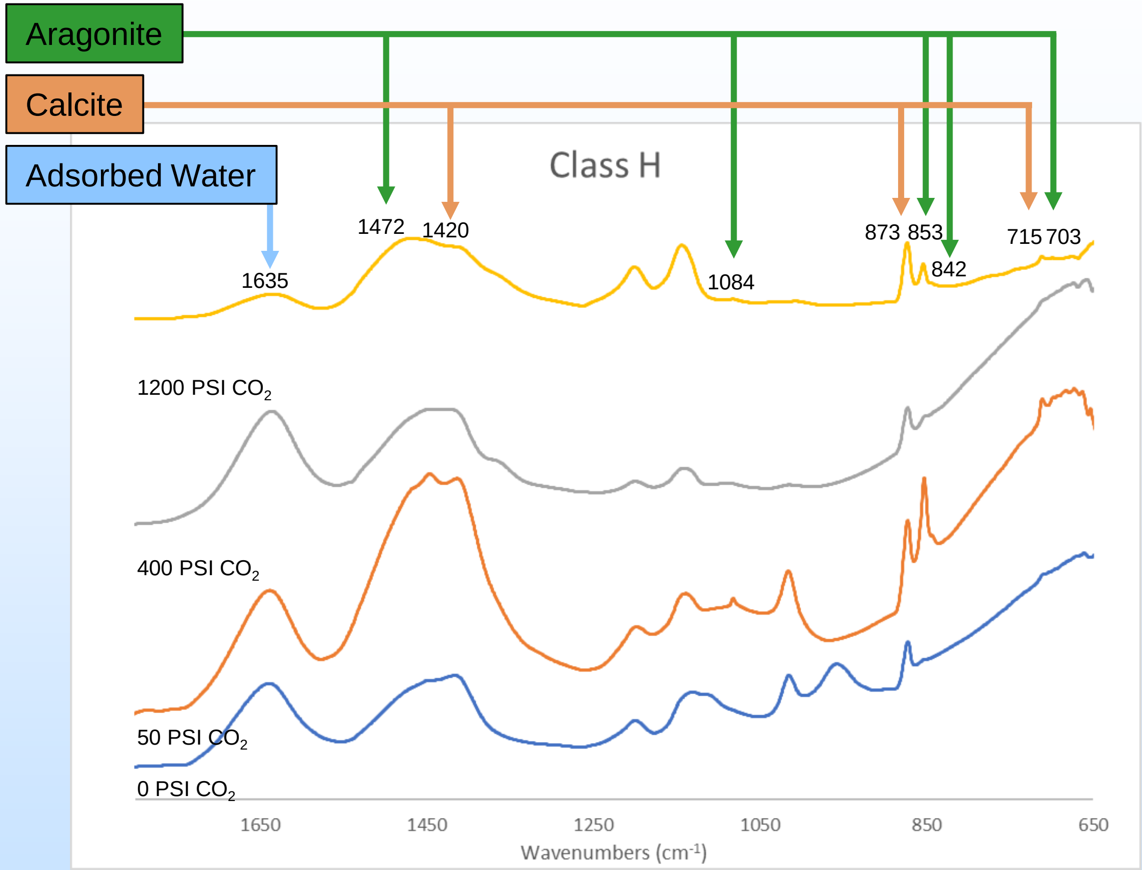
- The bubbles in the alteration zone are filled with calcium carbonate crystals
- These crystals have varying shapes that are representative of three polymorphs of calcium carbonate



Foamed Cement Image
taken by Meghan Brandi (NETL)

Weiss et al., 2014

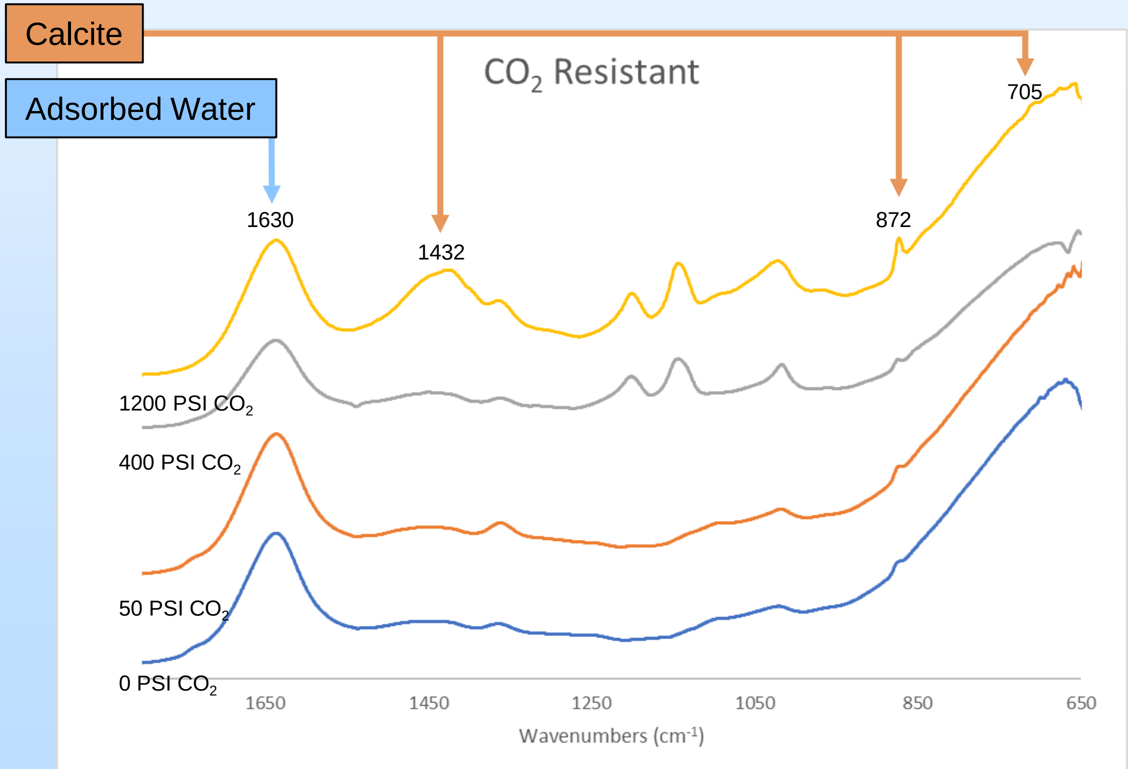
CO_2-Fluid-Cement Interface



Class H cement shows pressure-dependent polymorphs of calcium carbonate

CO_2 resistant cement did not show changes in the calcite polymorph structure

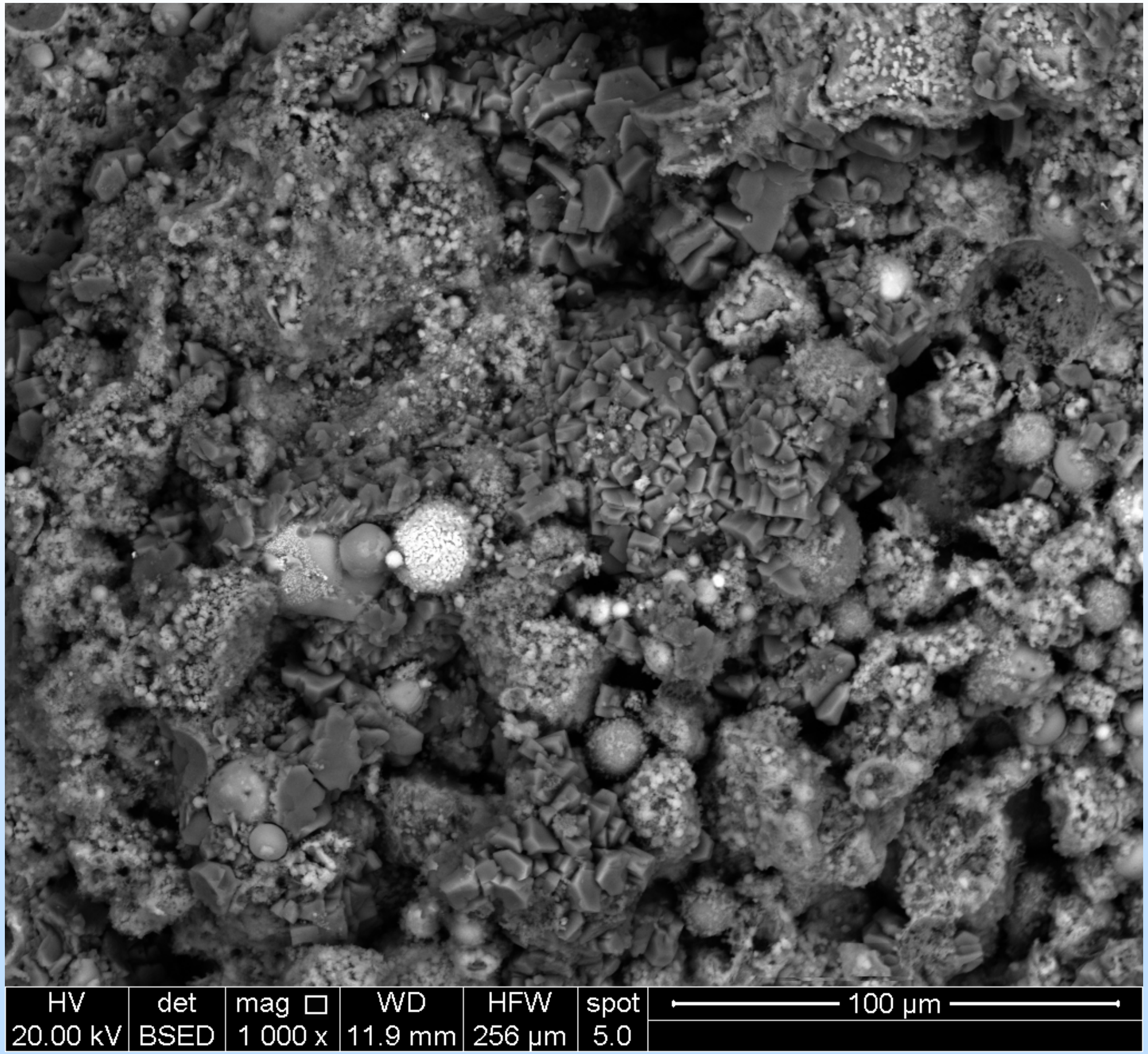
Although, vaterite was seen in the SEM, no characteristic peaks were present in the spectra

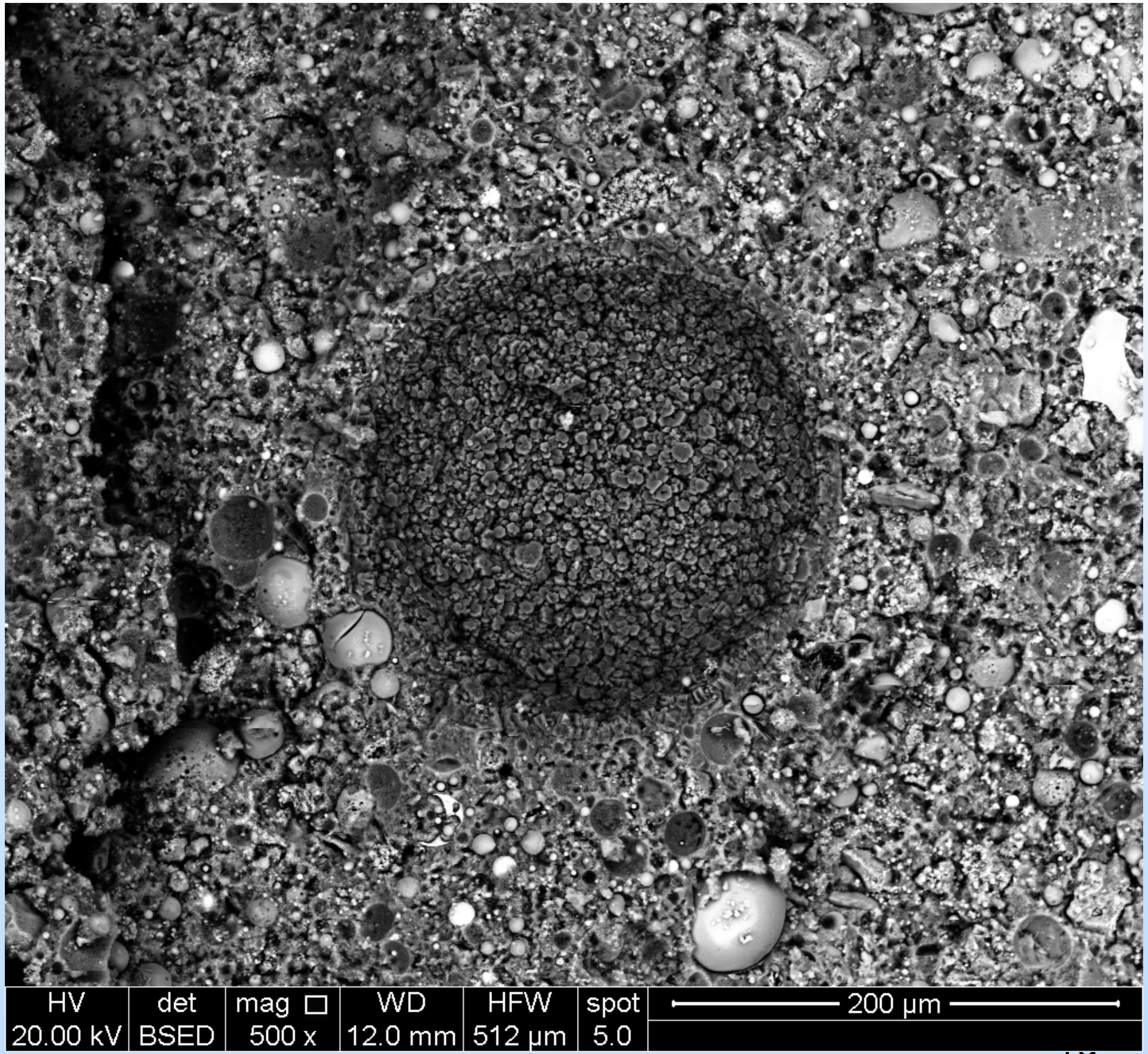


	v_3	v_1	v_2	v_4
Vaterite	1490, 1420	1085, 1070	870, 850, 830	750
Aragonite	1475	1080	855, 840	715, 700
Calcite	1430		870, 845	715

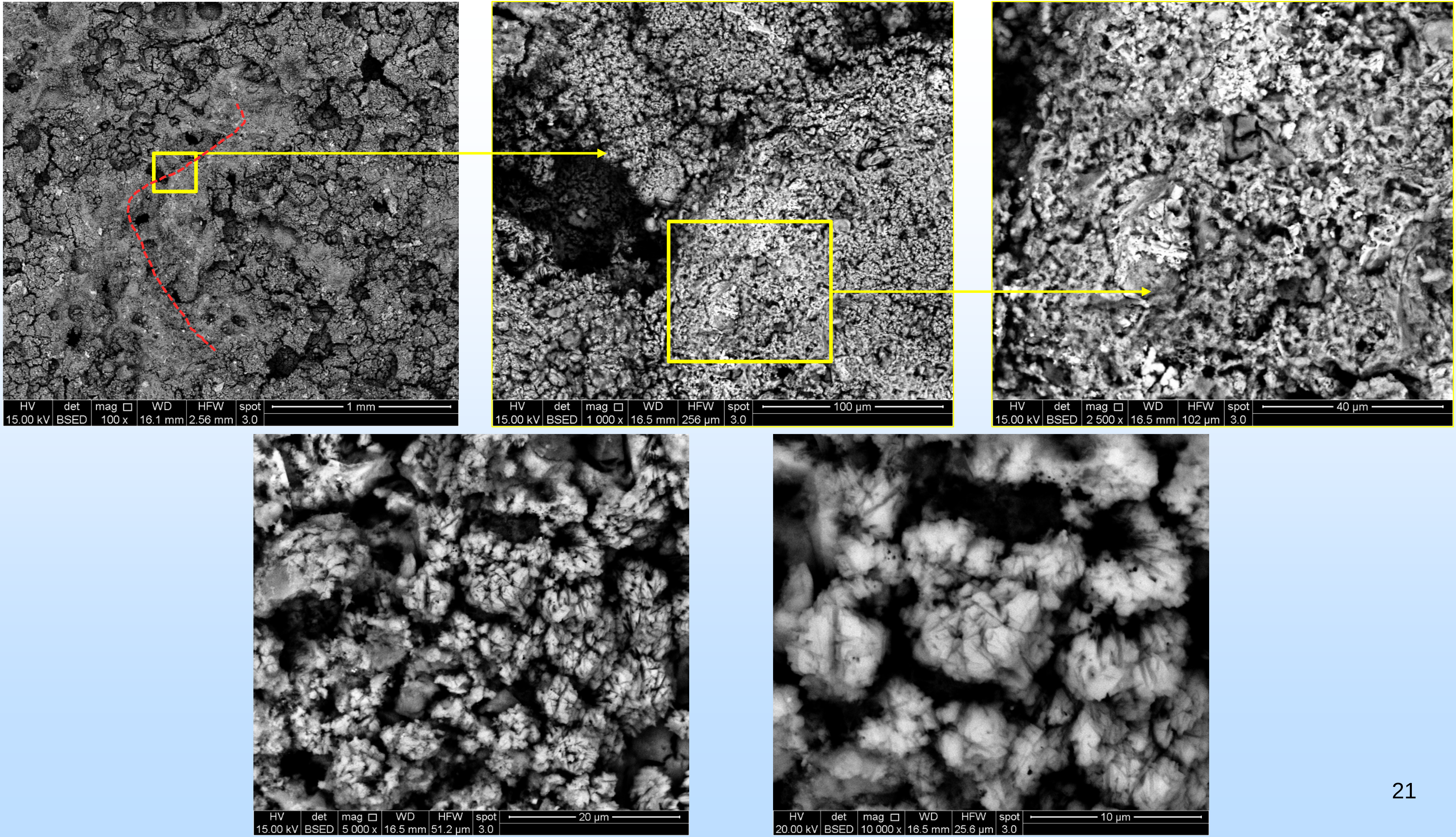
Zeitschrift für Kristallographie, Bd. 129, S. 405–410 (1969)

Future Work: CO_2-Resistant Cement





Questions?


HV det mag WD HFW spot
15.00 kV BSED 100 x 16.1 mm 2.56 mm 3.0
1 mm
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15.00 kV BSED 1 000 x 16.5 mm 256 µm 3.0
100 µm
HV det mag WD HFW spot
15.00 kV BSED 2 500 x 16.5 mm 102 µm 3.0
40 µm
HV det mag WD HFW spot
15.00 kV BSED 5 000 x 16.5 mm 51.2 µm 3.0
20 µm
HV det mag WD HFW spot
20.00 kV BSED 10 000 x 16.5 mm 25.6 µm 3.0
10 µm

Current Research Scope: CT Scanning

CT-Scanning Flow-through Experiments

Samples

- 20% Quality samples made in Pittsburgh (Rick Spaulding)
- Fractured using traditional Brazilian technique

Experimental Setup

- Flow Through
  I. Confining pressure = 1200 PSI
  II. Pore pressure = 800 PSI
  III. DI water at equilibrium with CO_2 as injected fluid (room temperature)
  IV. Flow rate of 0.2 ml/min for a period of ~260 hours
- CT Scanning
  I. Resolutions of 17 μm
  II. Scans taken as time permitted (no weekend scans)

ImageJ Processing

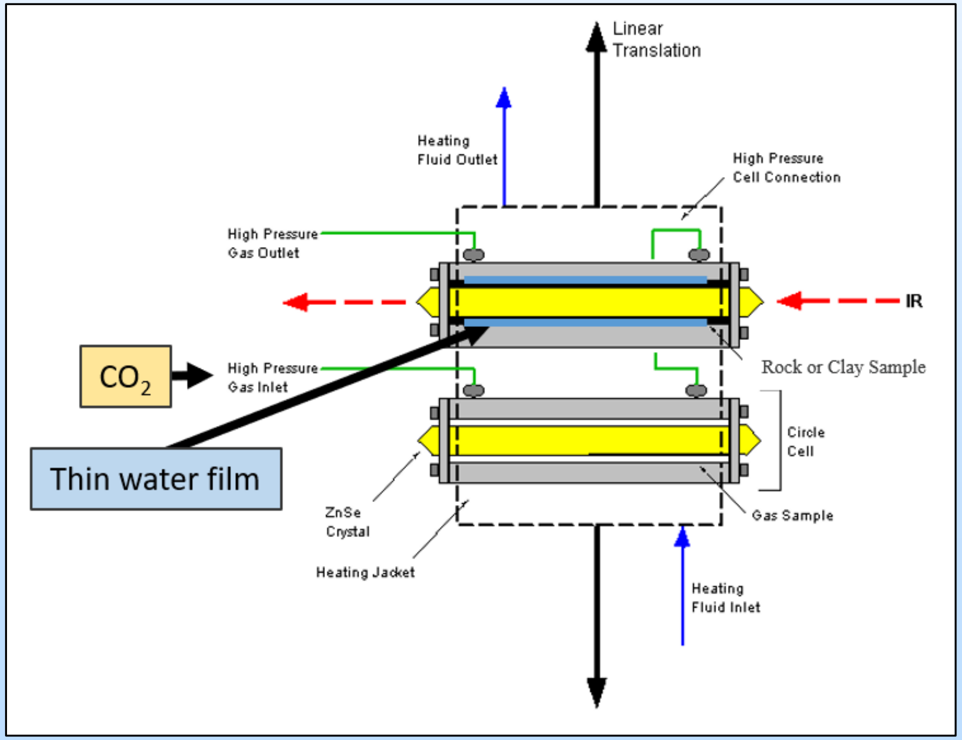
I. Images were scaled by 50% (reduction to 0.5 in X/Y/Z)
   - Size management critical to processing speed and efficiency

II. Images underwent bright outlier removal at 2 pixel radius

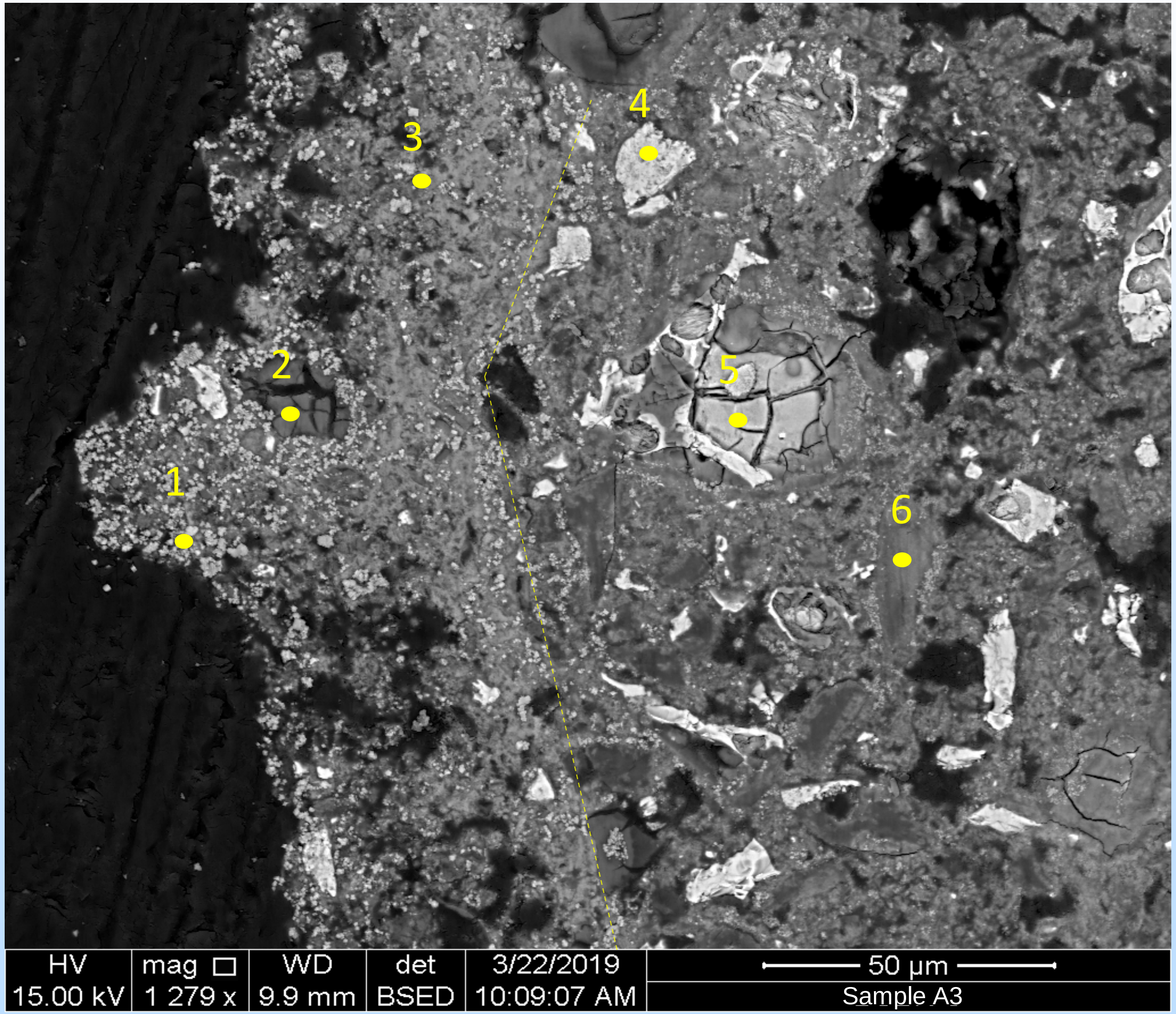
III. Images were then filtered using 2x2 mean (3-D)
   I. Processes facilitated easier segmentation & feature isolation

Current Research Scope: Fourier Transform Infrared Spectroscopy

- Samples: Class H cement and CO_2-Resistant cement
- Conditions:
  - CO_2-Fluid-Cement Interface
    - Samples prepared in Millipore water to create water film
    - 40°C and scanned at one pressure ranging from 0 to 1200 psig



OPC, cross section, sample A3



~50µm reaction depth at inlet

	p	Ca	Si	C	O	Fe	Mg	Al
$CaCO_3$	1	13.0	0.2	22.4	64.3	bd	0.2	bd
Mg-silicate	2	2.1	18.6	21.1	48.2	0.3	9.0	0.5
More Ca	3	16.1	7.7	18.3	54.0	0.2	3.2	0.53
Al and Fe	4	19.2	2.1	bd	60.7	8.4	2.0	7.6
unhydrated	5	25.5	8.8	11.6	52.6	0.3	0.8	0.4
Less Ca	6	10.9	11.6	16.4	58.4	0.5	1.5	0.4

Atomic%