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# Mechano-Chemical Interactions within Engineered Barrier-Geomaterial Interfaces

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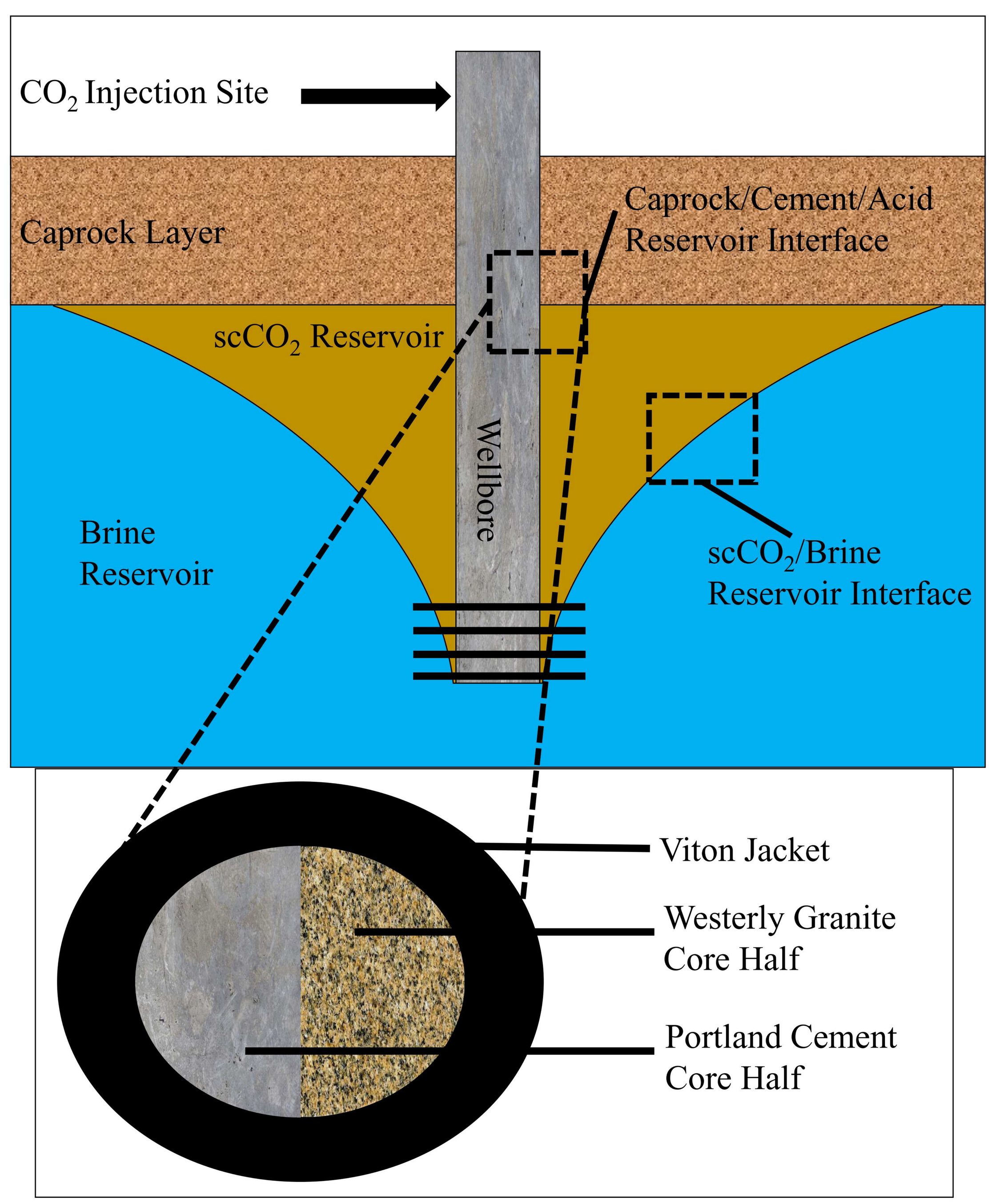
## Introduction

Coupled chemical and mechanical interactions can lead to leakage pathway development at cement-geomaterial interfaces, reducing the effectiveness of engineered cement barriers against acidified leakage contaminants.

We examine chemical-mechanical interactions, acoustic coupling, and pathways to failure in controlled triaxial benchtop experiments, which monitor real-time cement-granite interface degradation in situ by ultrasonic and chemical methods, and pre- and post-experiment using microindentation and microCT imaging. Full waveform analysis shows a decrease in a fracture interface wave speed indicating a reduction in fracture specific stiffness likely following portandite dissolution from the surrounding cement matrix, followed by an increase stiffness as the experiment progresses. The sensitivity of the interface wave to fracture conditions make these modes a potential tool for the detection of interface alteration in wellbores. Tomographic images show detailed development of three-dimensional leaching patterns involving reaction fronts migrating from the interface as well as wormhole development within the interface.

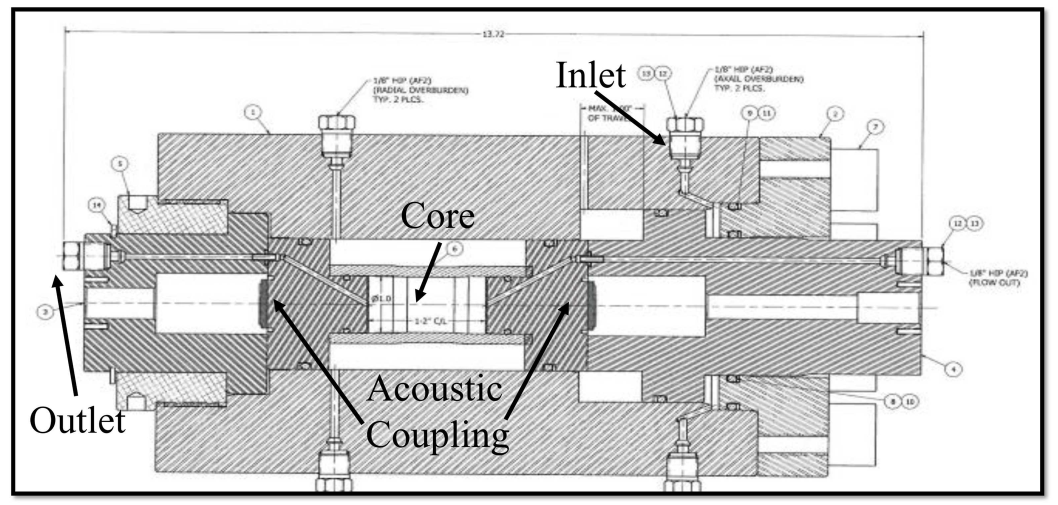
Results are being used to validate a coupled computational fluid dynamics/mechanics code. Future plans call for using the validated coupled chemo-mechanical model specifically in analyzing the spatio-temporal evolution of other types of interface alteration including carbonation and sulfonation, and in general as a predictive tool for assessment of cement barrier integrity.

## Small-Scale Wellbore Integrity Study

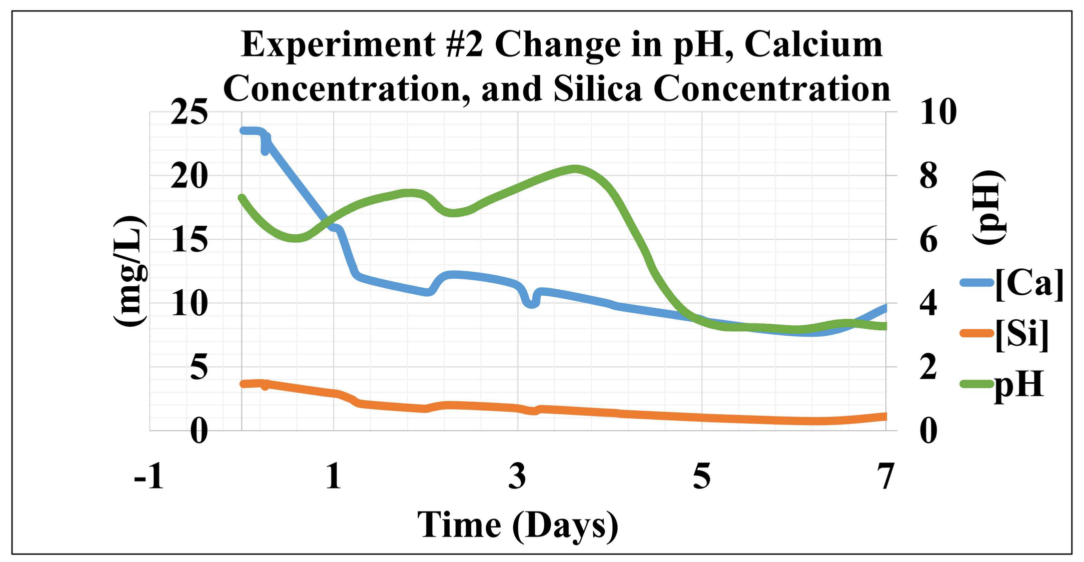



A two inch in length and one inch in diameter core made half of Type G cement and half of granite was fabricated to make a representative sample of the caprock/cement interface. The sample was wrapped in Teflon and then loaded into a Viton jacket, which was then inserted into a pressure vessel for fluid flow and acoustic testing.

## Flow Through Experiments

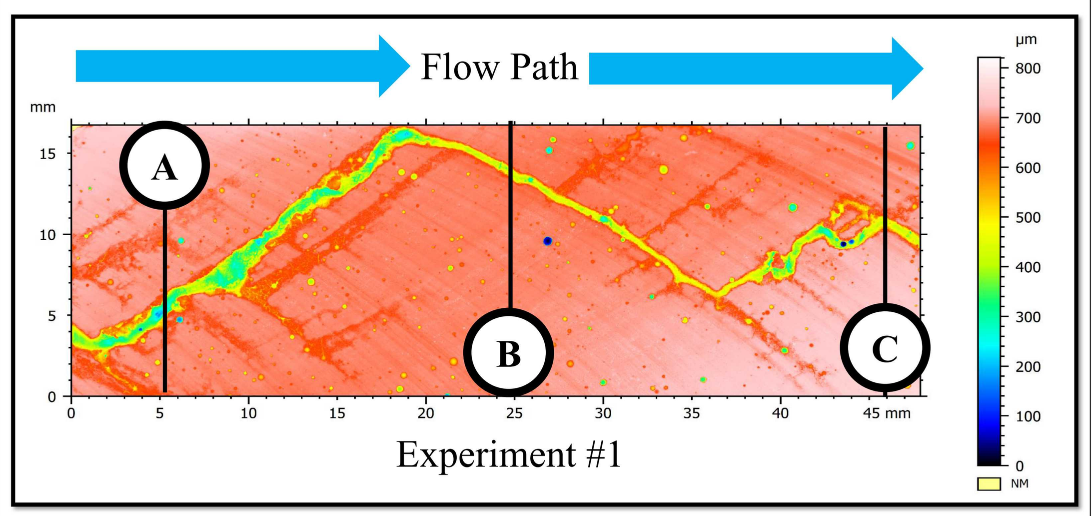



A core-holder with ultrasonic transducers was used to simulate wellbore conditions by providing a constant confining pressure of 13.3MPa, an axial load of 16.8MPa, and a temperature of 65°C. All data was recorded and saved in a data logger. A syringe pump flowed pH 3.1 HCl acid through the cement granite fracture at.4mL/min. The pH of the effluent solution was recorded with an inline pH probe. P &S waves were recorded throughout experiment.

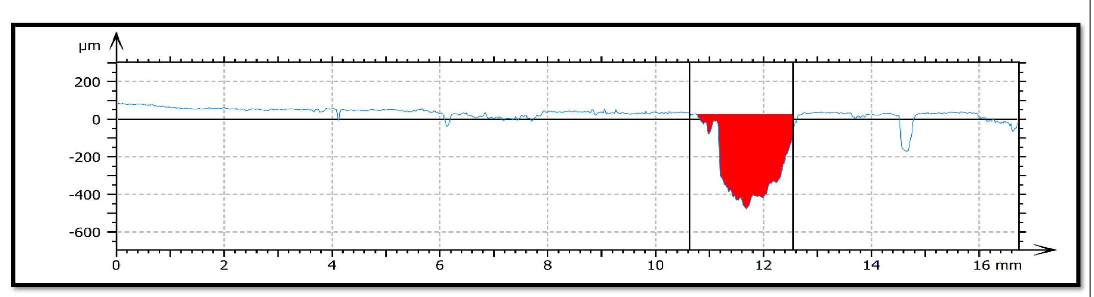



The initial surface reaction between the HCl and cement caused the pH and the [Ca] to rise. Eventually, the reaction became diffusion controlled causing the dissolution rate to decrease.

## Surface Analysis - Profilometry

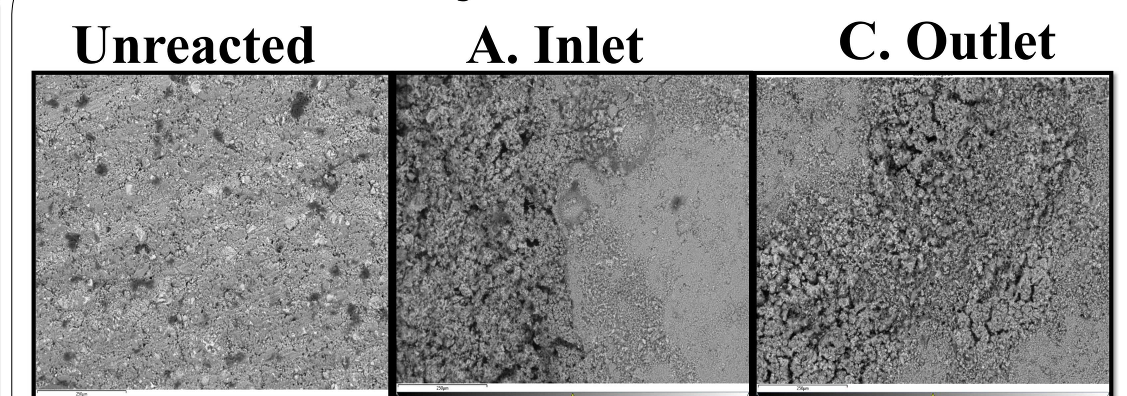



A Nanovea ST400 Profilometer was used to capture the surface roughness of cement before and after being flooded with HCl. The results show a wider deeper channel at the inlet with the channel narrowing and decreasing in depth as the channel migrates further from the inlet. Additionally, the scan shows smaller channel paths, cutting marks, and some pore features.



Channel A, pictured above, is 510µm deep, 555652 µm² large, & 2mm wide. B is 310µm deep, 156318µm² large, & 1mm long. C is 313µm deep, 274709µm² large, & 2.5mm long.

## Surface Analysis – SEM and EDS




In the presence of water, HCl will self-dissociate into its hydrogen and chlorine atoms. Cement is susceptible to corrosive attacks. At the cement-surface-reservoir interface, hydrogen atoms initiate a reaction propagation front with the calcium hydroxide in the cement. This causes the calcium hydroxide in the cement to dissociate into its calcium and hydroxide atoms. The free calcium then bonds with the free chlorine atoms forming calcium chloride.

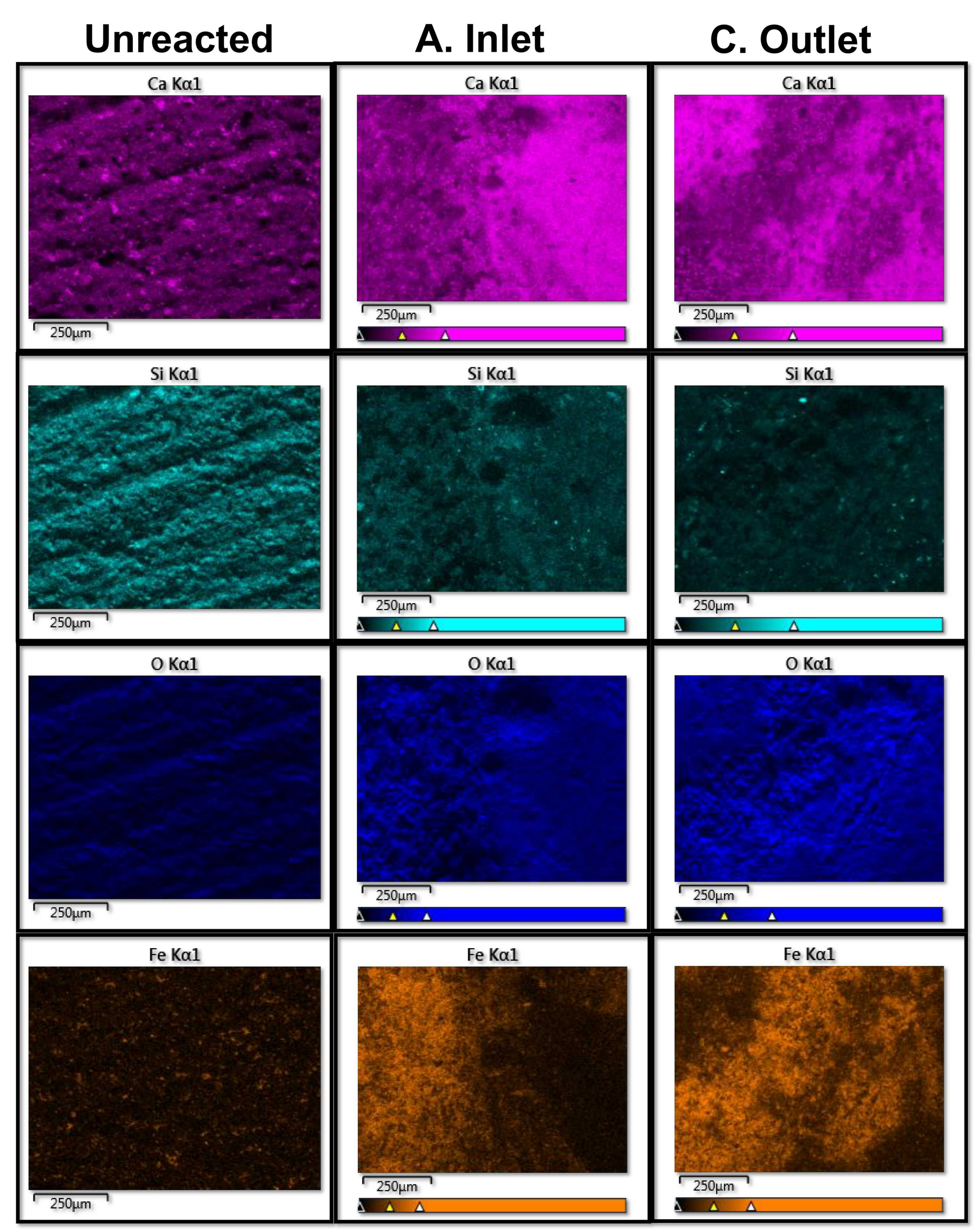
$$HCl \rightarrow H^+ + Cl^-$$

$$Ca^{2+} + HCl + OH^- \rightarrow CaCl_2 + H_2O$$

$$H^+ + CaCl_2 \rightarrow Ca^{2+} + HCl$$

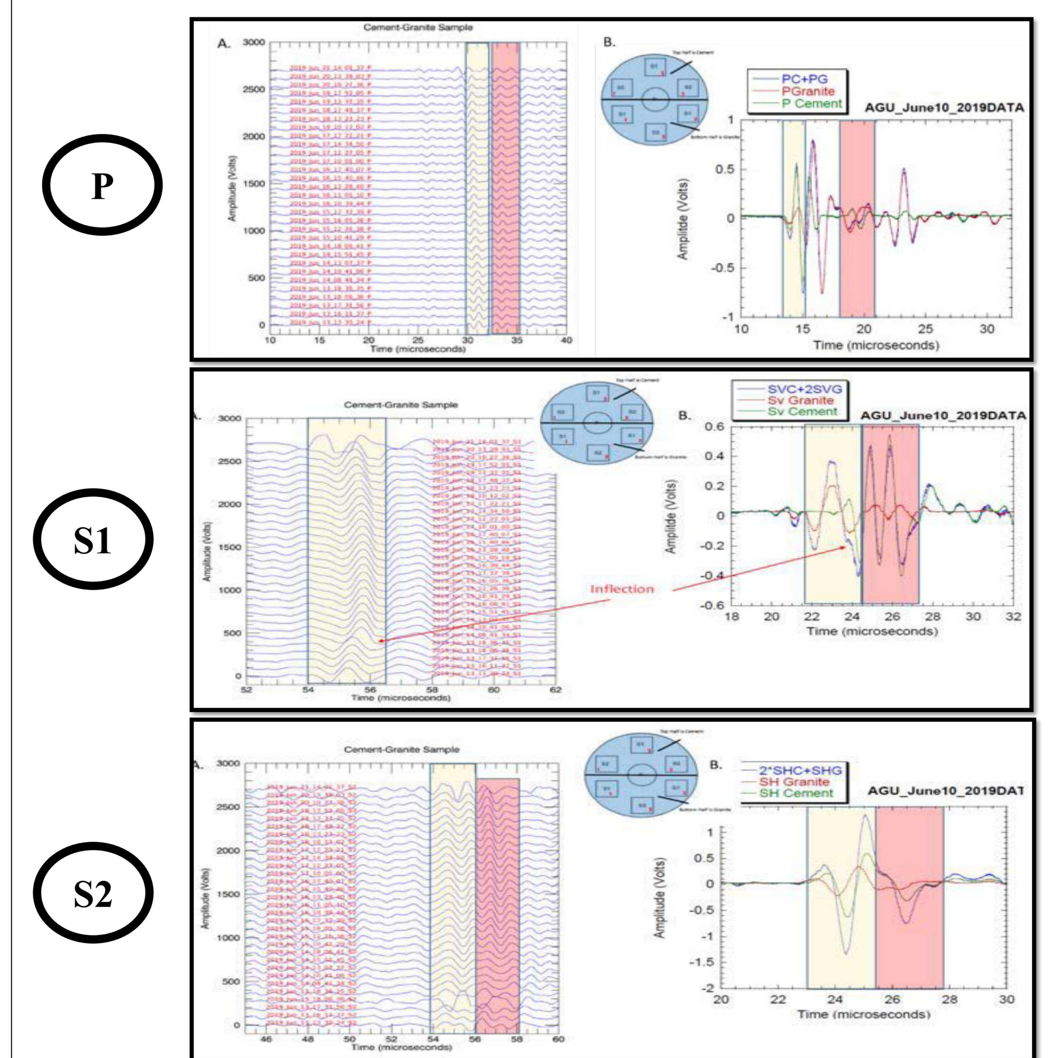
$$CSH \rightarrow Ca^{2+} + OH^- + SiO_2$$

The calcium chlorine precipitant reacts with free hydrogen atoms, further dissociating into free calcium and chlorine causing an orange calcium leached layer to form. Eventually, the Calcium Silica Hydrate in the cement will degrade leaving behind an amorphous silica gel layer which has been known inhibit further cement degradation.

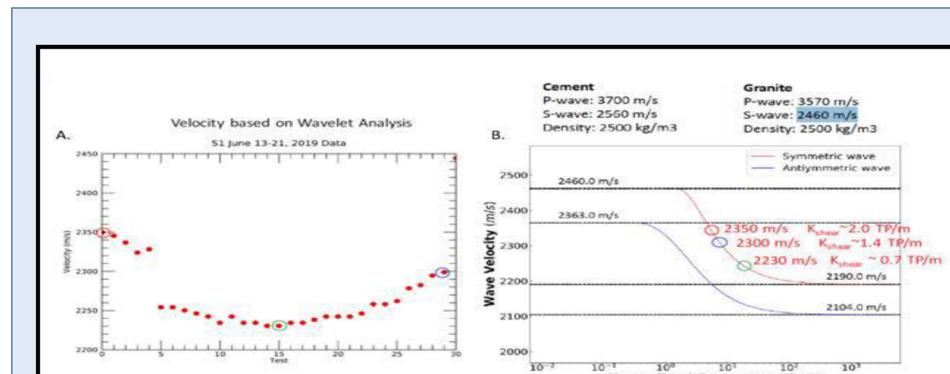



The results show a decrease in Ca and Si in the channels with an increase of Fe and O in the channels. The Fe and O are likely responsible for the orange coloring left behind in the channel's flow path.

## Ultrasonic Analysis




- **Top:** First arriving P wave (yellow region in the figure), and second arrival (rose region) are consistent with measured responses from solid cement samples.
- **Middle:** Yellow region is consistent with the Rayleigh phases (the interface or guided waves through the cement-granite microannuli in the compressed system) for granite measured outside the core-holder system. The first arriving S1 is dominated by the granite system until the fifth waveform (shown by red arrow), showing an inflection which might indicate a coupling between the two surfaces of cement and granite in the compressed state.
- **Bottom:** The rose region in the figure to the right, taken for the uncompressed microannuli measured outside the core-holder system, indicates a waveform only present in the uncompressed system and was not observed for the Test 2 sample under compression. For the polarized S2 waveforms plotted in Figure 2-10, the yellow demarcated region can be either granite, cement, or a combination of both. The rose region is consistent with wave components from the cement phases.



During the course of Test 2, the interface wave velocity is observed to decrease in the first three days of the test, but then shows a slight recovery, possibly due to creep closure. These results suggest that interface waves can detect microannuli degradation.

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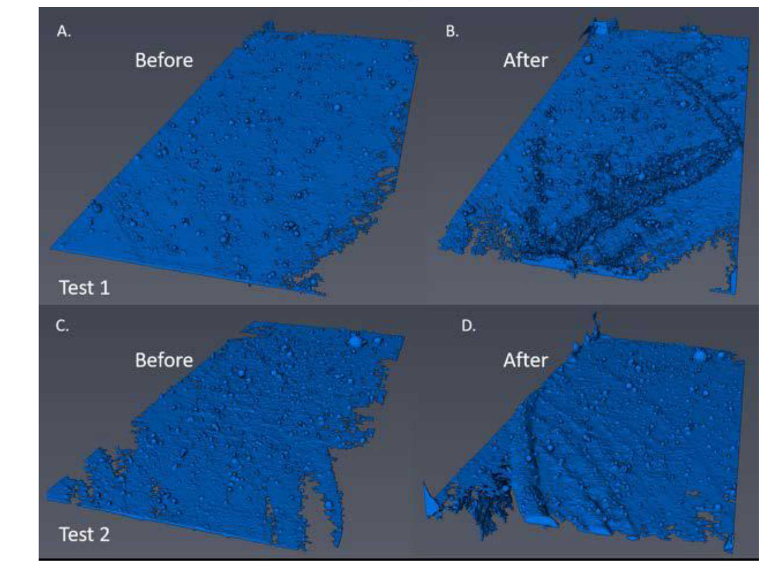
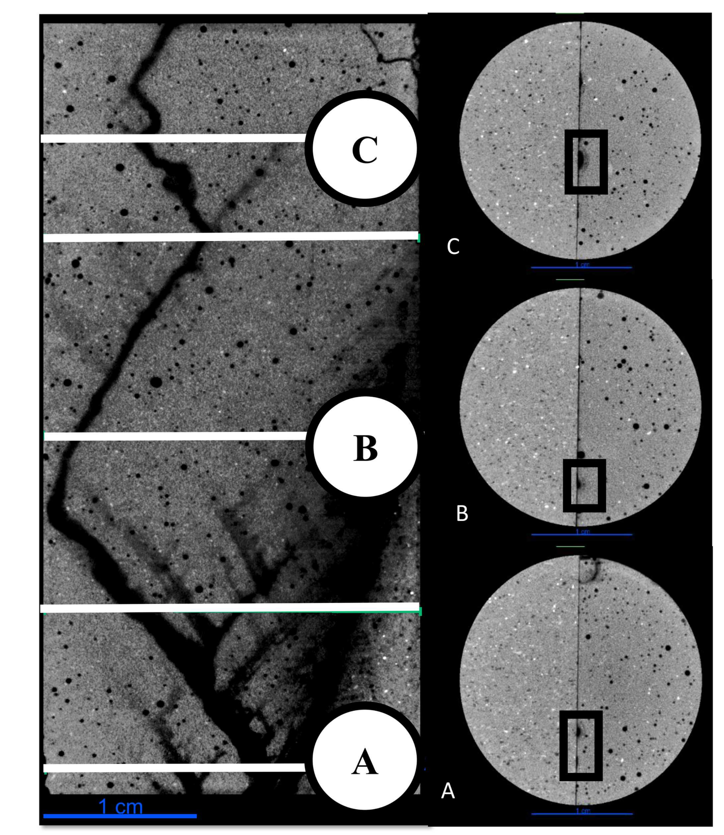
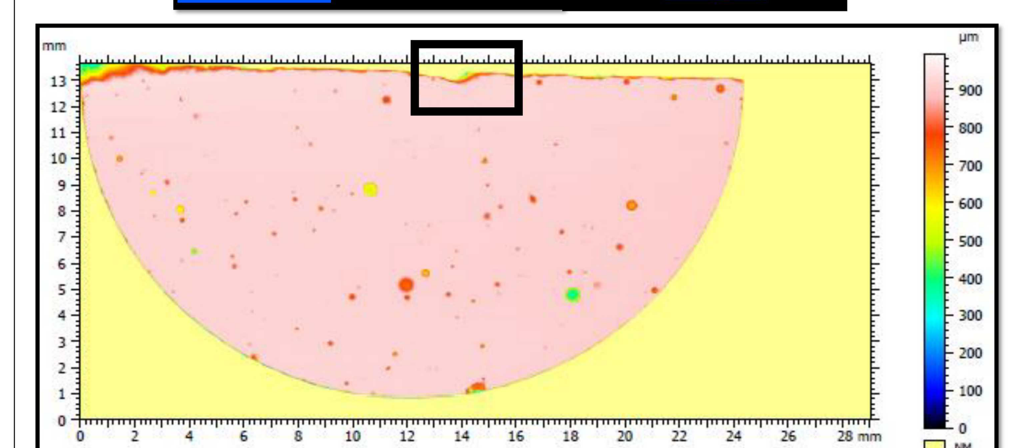
## On-Going Work




CT scanning was performed before and after each flow through experiment. Reconstruction involves meshing for CFD and other modelling efforts.



These channel sections will be micro-indented at Vanderbilt University to determine changes in hardness and elastic moduli as a function of distance from the channel.

## Conclusions

The ultimate goal of this research was to see if we could capture an acoustic response in the cement as it reacted with an acidic medium. The benchtop flow through experiments replicated wellbore conditions where acid migrates through the caprock-cement interface. ICP-OES and pH data shows an initially fast reaction which slows down as the Ca is leeched away. The acoustic data shows a change in the shear waves pulsing through the cement as the cement was degraded. The waveforms also show a gradual relaxation with reaction progress. The SEM and EDS analysis show that Ca and Si are greatly depleted in the channel pathways compared to unreacted cement. Lastly, indentation analysis will be done to see how the cement's hardness changed during the experiments. All of these results suggest that ultrasonics may be an effective tool to detect early signs of corrosion in wellbore microannuli.