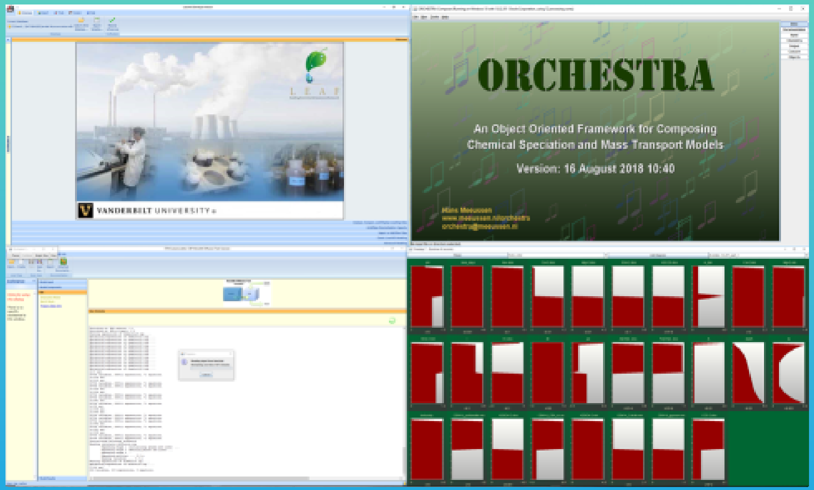
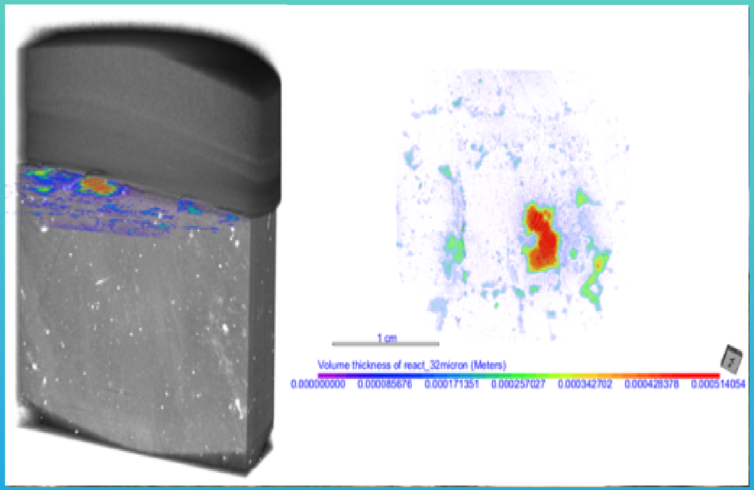
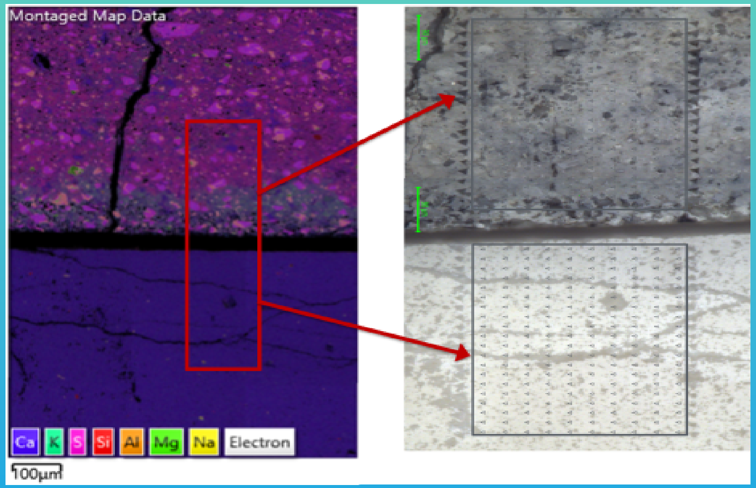
SAND2021-6117C

Spent Fuel and Waste Science and Technology (SFWST)







NUCLEAR WASTEFORM AND BARRIER MATRIXES INTERACTIONS WITH GEOLOGIC STRATA

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Objectives

Project goal: Characterize interactions of doped cement materials (Low pH cements and CEM I) with carbonate geologic strata (e.g., limestone, marl, chalk, oil shale).

Specific objectives:

i) Use laboratory experiments to characterize the reactions and transport of radionuclides (dopants) and primary matrix constituents at the interface between carbonate rock types and cementitious barriers; and,

ii) Demonstrate and benchmark multiphase diffusion reactive transport models for parameter estimation and to simulate long-term interactions considering potential intermediate depth borehole disposal.

Project Approach

Rocks and cement characterization – ***porosity, mineral assemblages***

1313 tests (L/S = 10 and 1 over range of pH) – ***calibration of mineral reaction set***

1315 tests (diffusion) – ***calibration of tortuosity, verification of mineral reaction set***

measured

Completed

Cement/rock interface modeling - prediction

planning

Data from cement/rock interface experiments

measured

comparison

Solids characterization – micro-CT, Nano-indentation, SEM, LA-ICP-MS

Interface Evaluations

- 6 rock types, each with 2 cements
- Experiments – ca. 1-2 years
- Simulations

  Experimental planning

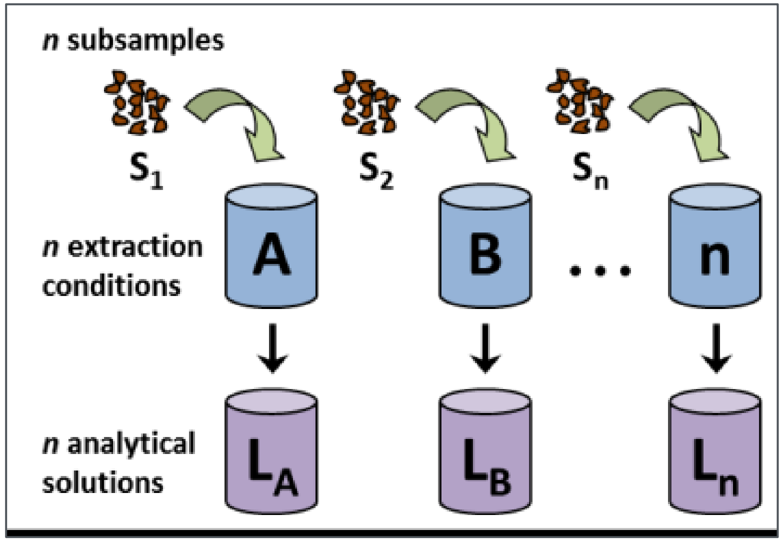
  Experimental data interpretation

  Long-term prediction

EPA Method 1313

Method 1313

- pH dependent leaching test
  - L/S (ml g^{-1}) of 10 and 1 for rock samples and two cement types.
  - 10 parallel extractions at different target end-point pH
- **Analysis**
  - Extracts analyzed using ICP-OES, ICP-MS, TOC, and IC. Additional measurements include pH, conductivity.



Mineral Reaction Set Calibration

Data from USEPA Method 1313

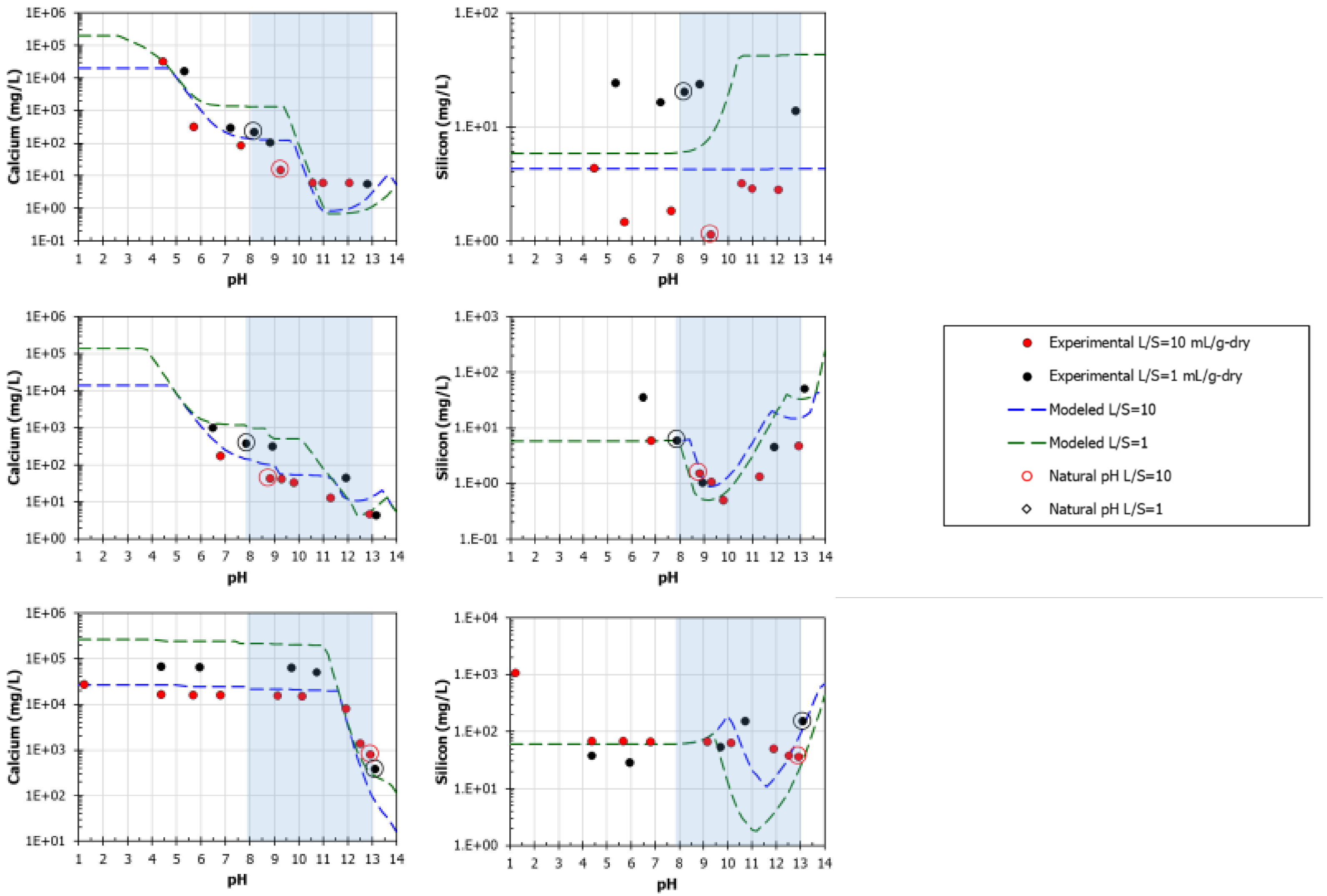
Ca

Si

Limestone

Marl

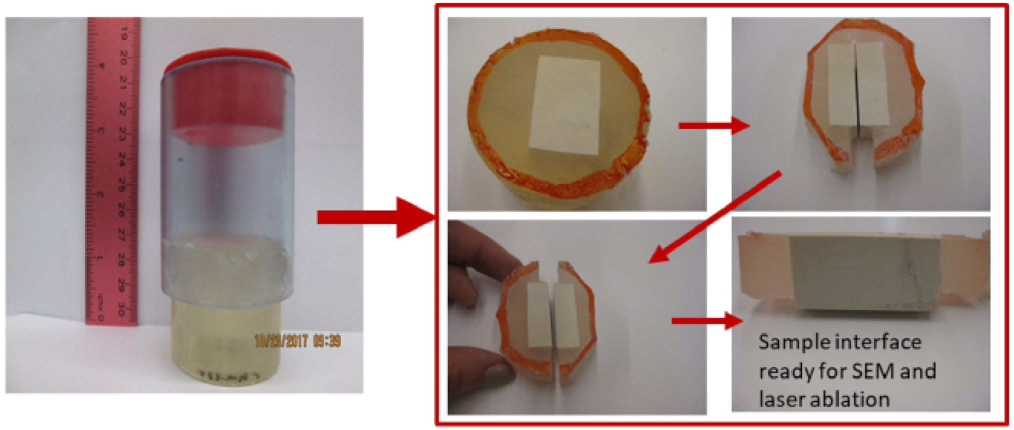
OPC paste



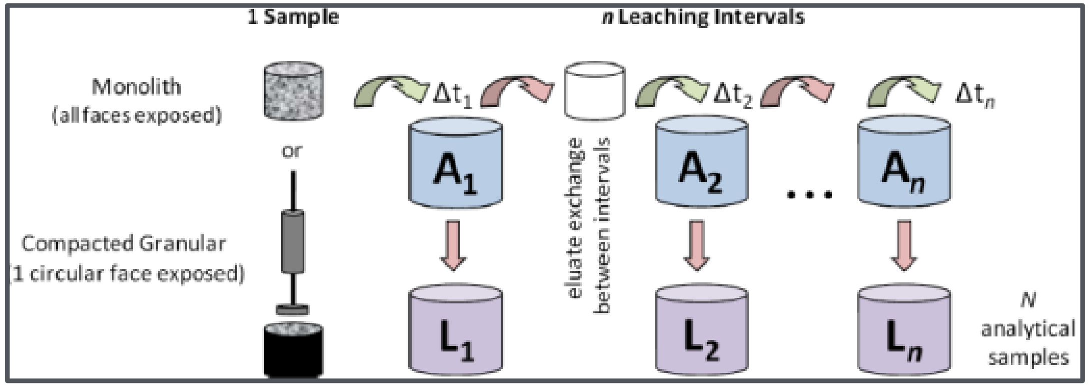
Experimental Methods (EPA 1315)

Method 1315

- Mass transfer rate tank leaching test - modified for post-test profile characterization

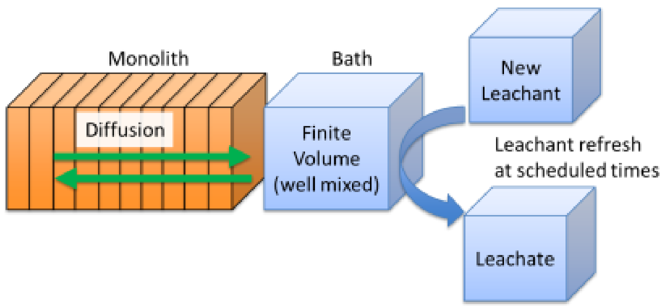


Method 1315 – Experimental set up and sample processing

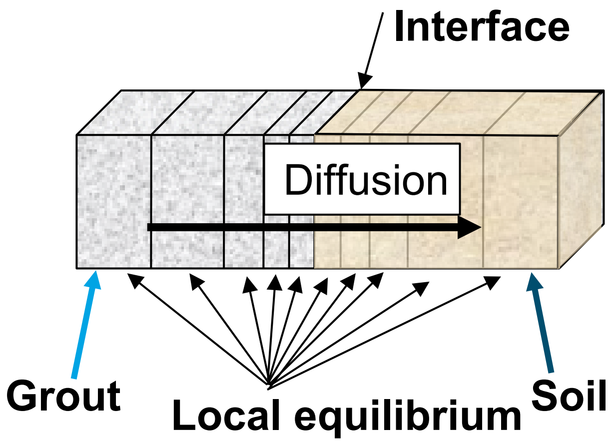


Comparison of Diffusion Leaching Test to Field Conditions

Test Conditions



Simulation Conditions



<u>Diffusion Leaching Test</u>

- 10 mL/cm^2 liquid volume-to-surface area (L/S_A)
- Leachant refreshed frequently to maximize leaching (dilute boundary condition)
- Saturated conditions

<u>Field Conditions</u>

- ≈0.02 to 0.1 mL/cm^2 liquid volume-to-surface area (L/S_A), based on saturation
- Unsaturated conditions; slow porewater displacement

➢ **Leaching under field conditions is several orders-of-magnitude slower than lab test conditions**

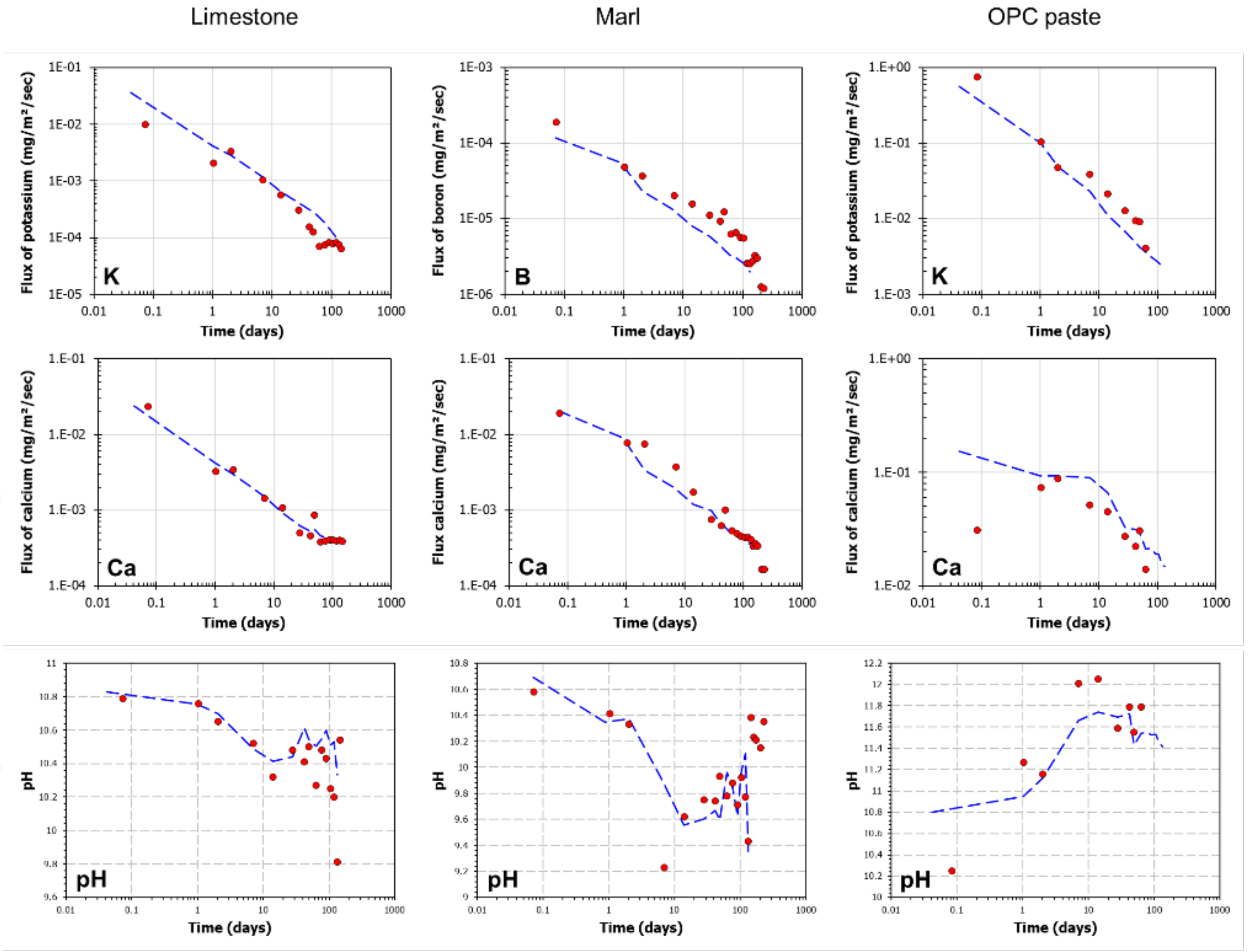
Tortuosity Calibration

Calibration and Validation of mineral reaction set

Prediction of 1315 results based on mineral reaction set calibrated by 1313 test

calibration

Validation



$$\frac{porosity}{tortuosity} = \frac{\emptyset}{\tau^2} =$$

0.0007 | **0.003** | **0.0006**

Interface Experiments

Current Status:

Cements were cast on **saturated** rock (Oct. 2019)

6 rock types - limestone, chalk, marl, oil shale, LOM and HOM

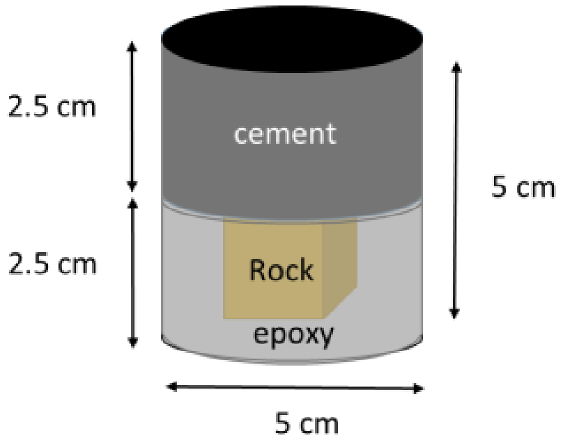
2 cements - OPC and low pH cement

6 samples per rock/cement interface

Curing and aging conditions:

30 °C and 100% relative humidity

Sampling time to be based on simulation & micro-CT results

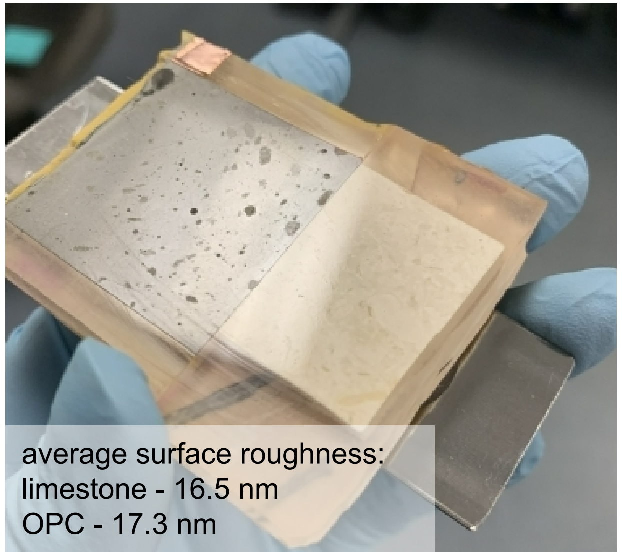


Current curing time: ~12 months

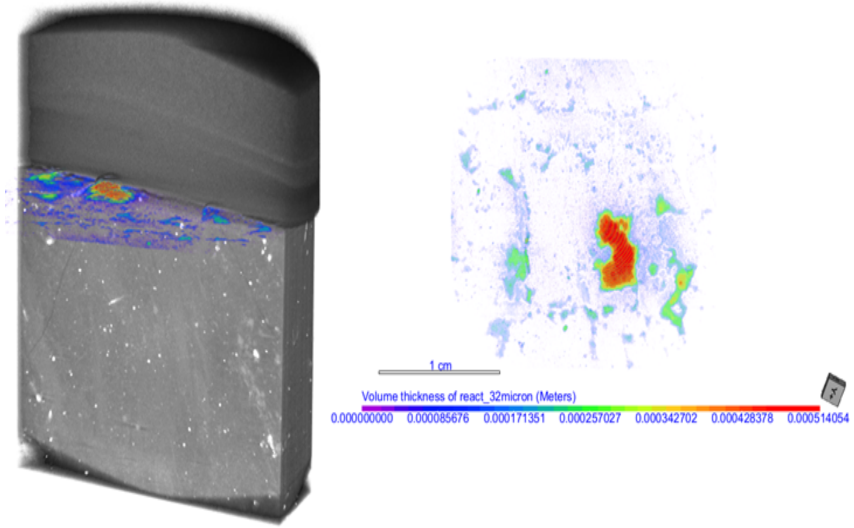
Advanced Characterization of Interfaces

Interfaces are characterized for:

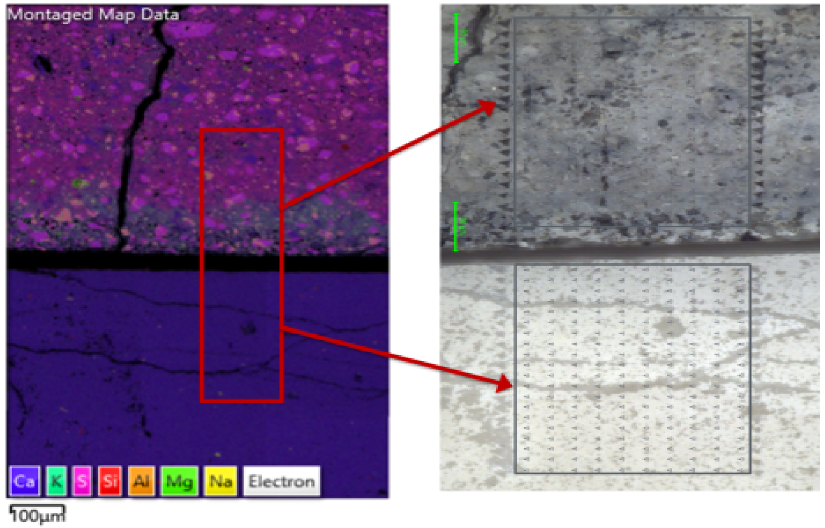
- Leaching and interface characterization – SEM-EDS and LA-ICP-MS
- Volume and porosity change - micro-CT
- Changes in material mechanical properties as a result of interface reactions - Nano indentation



Polishing

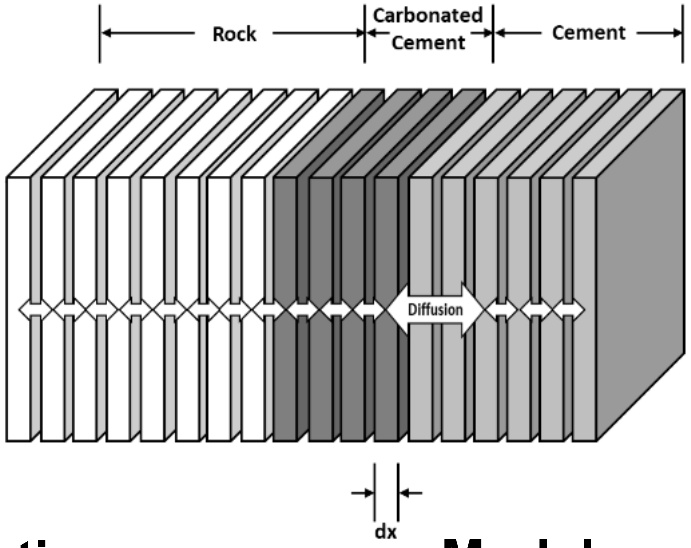


Micro-CT



SEM-EDS **Nano-identation**

Conceptual Model – Rock/Cement interface



Model assumptions:

- Each cell is well mixed
- Local equilibrium
- C-(N-)A-S-H solid solutions
- Multi-ionic diffusion only

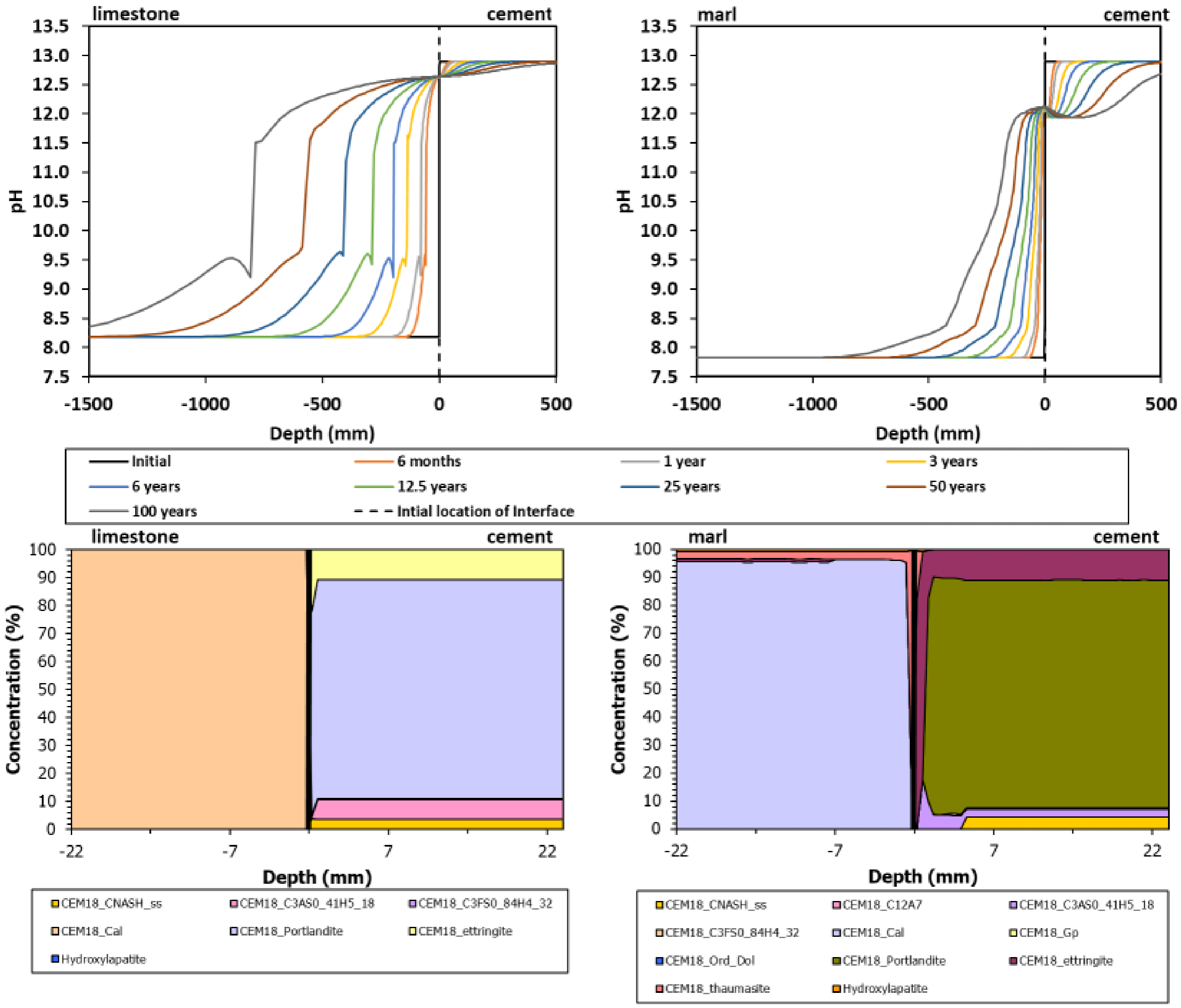
Modeling platforms:

- LeachXS/ORCHESTRA
- PFLOTRAN

Model conditions for experimental case:

- 100 years simulated, saturated conditions, 30 C
- 1-D, 378 cells, Finite volume
- No fluxes at external boundaries
- Thermodynamic databases – Minteq v4; LLNL, CEMDATA18 (Lothenbach et al. (2018))
- Initial carbonate content – based on 1313 test
- Tortuosity – calibrated values
- Porosity – measured values

Interface Models Results



Interface Models Results – carbonation front progress prediction

The location, X_C , of the moving carbonation front as a function of cement composition and conditions, when the relative humidity is above 50%, is (Papadakis et al., 1989):

$$X_c = A\sqrt{t}$$

$\boldsymbol{X_c}$ - the location, of the moving carbonation front (mm)

A - proportionality constant (mm $yr^{-0.5}$)

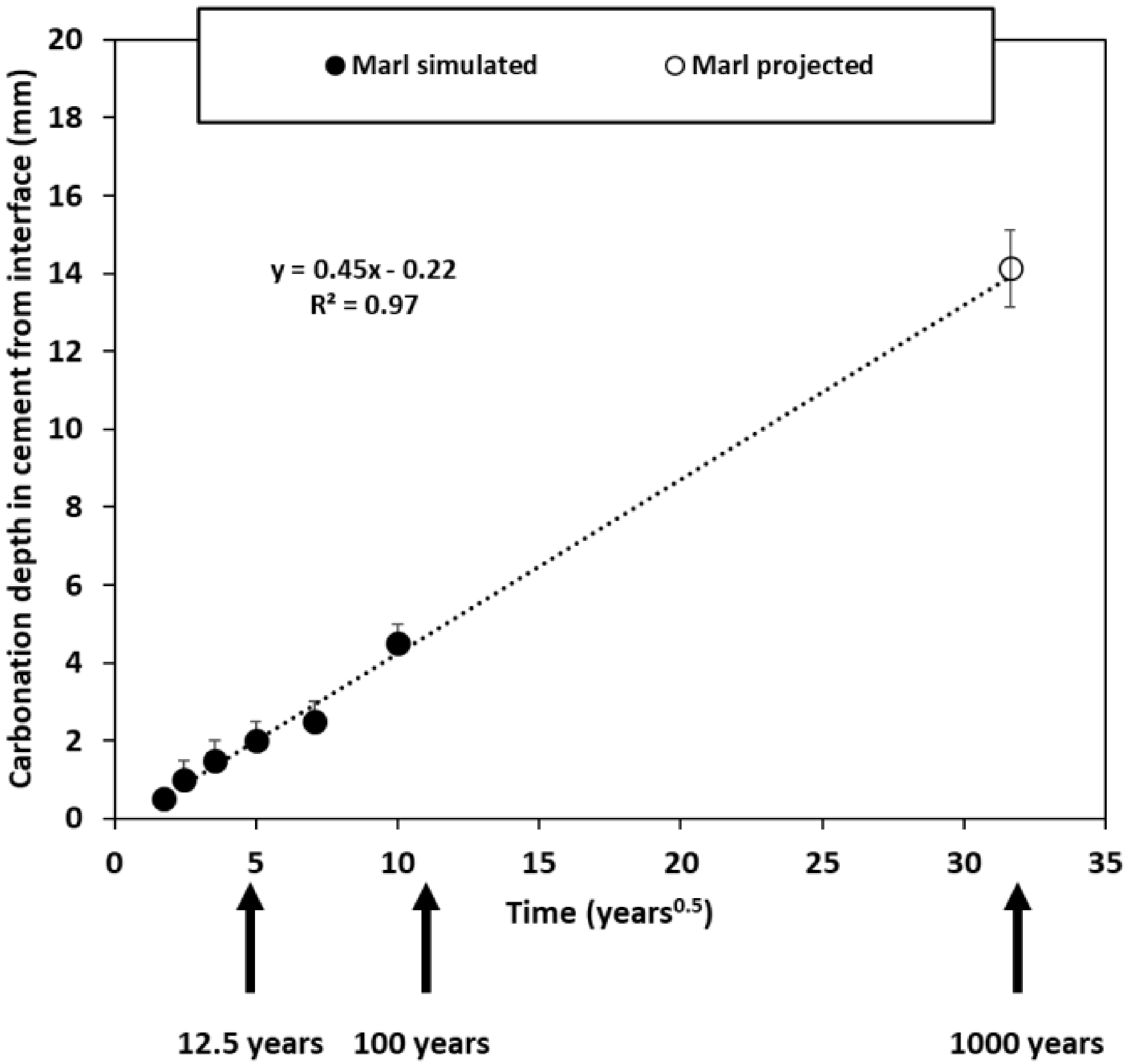
t - time (years)

1,000 years scenario (saturated):

- **14** mm OPC are carbonated

10,000 years scenario (saturated):

- **45** mm OPC are carbonated



Interface Models Results – effect of water saturation

- water relative saturation in vadose zone: 10%-40% at depths deeper than 2m
- The diffusivity under saturated conditions is about 21 and 2150 time greater than at 40% and 10% water relative saturation, respectively.
- Incorporating these factors into the proportionality constant (*A*) results in:
  - under 40% water relative saturation: 435,000 years and 4.5 million years for the carbonation front to penetrate to a depth of 14mm and 45mm (from 1,000 and 10,000 year scenarios) into cement.
  - Under 10% water relative saturation, 4.5 million years and 46 million years are required to penetrate depth of 14mm and 45mm.