VANDERBILT UNIVERSITY

Sandia National Laboratories

SAND2019-13810C

National Nuclear Security Administration

NUCLEAR WASTEFORM AND BARRIER MATRIXES INTERACTIONS WITH GEOLOGIC STRATA IN THE SUBSURFACE OF THE YAMIN PLATEAU, NORTHERN NEGEV, ISRAEL

Israel: [1]Gabriela Bar-Nes (PI), [1]Erez Boukobza, [1]Yonatan Harnik, [1]Ofra Klein-BenDavid

United States: [2]David Kosson (PI), [2]Chen Gruber , [2,3]McKalee Steen, [2]Kevin Brown, [2]Rossane Delapp, [2]Andrew Garrabrants, [2]Lesa Brown, [2]John Ayers [3]Ed Matteo, [3]Carlos Jove-colon

The Netherlands: [4]Hans Meeussen

[1]Nuclear Research Center, Negev (NRCN)

[2]Vanderbilt University (VU)

[3]Sandia National Laboratory (SNL)

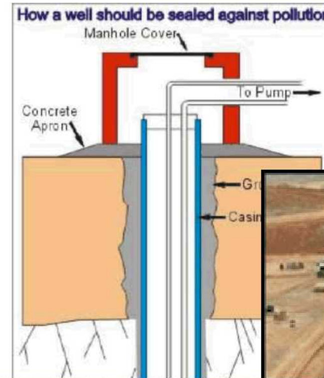
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Presentation Outline

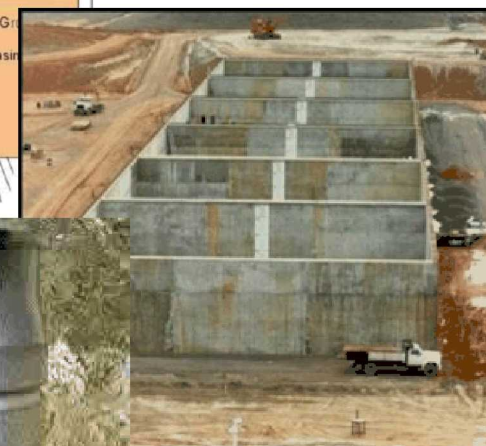
- Objectives
- Expected Contribution to Intermediate Depth Borehole (IDB) Design and Safety Case
- Project Approach
- Key Characterization Results
- Reactive Transport Benchmark Case
- Reaction Set Selection and Thermodynamic Model of Materials
- Interface Simulation Results
- Interface Experiments
- Future Directions

Cementitious Materials and Carbonate Rocks

- Cementitious materials are widely used in many applications of radioactive waste (IAEA 2013 TECDOC):
    - Deep-intermediate borehole disposal
    - Waste forms
    - Seals for retarding waste transport
    - Engineered barriers
    - Construction assemblies



http://www.briodydrilling.com/services/borehole-grouting-by-tremie-pipe-method-including-use-of-well-grouting-band-8



http://cementbarriers.org/applications/

https://goo.gl/images/Nm2P9a

- Cement interactions with the surrounding lithology will create a **highly alkaline local environment**, which may cause alteration and impact radionuclide transport.

Expected Contribution to IDB Design and Safety Case

- Define the chemically appropriate cement formulation for the host rocks in Israel
- Provide mechanistic basis and validated models for reactions and diffusive mass transport at representative rock-cement interfaces
- Define expected contaminant migration factors (e.g., effective R and K_d) from cement waste form to rock formation
- Provide input on the safety margin for unsaturated cement environment (strength, formulation and migration)

Objectives

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

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 multiphase diffusion reactive transport models for parameter estimation and to simulate long-term interactions considering potential future disposal in different Negev geologic formations.

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

Data from cement/rock interface experiments

comparison

Cement/rock interface modeling - prediction

Interface Evaluations

- 6 rock types, each with 2 cements
- Experiments – ca. 1-2 years
- Simulations
  - Experimental planning
  - Experimental data interpretation
  - Long-term prediction

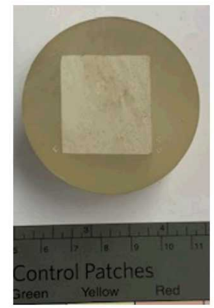
Test Materials

Cements

Rocks

CEM1 (OPC)

Marl



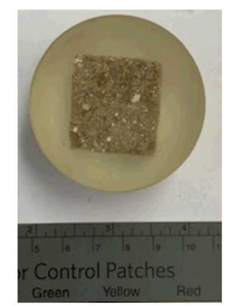
Chalk

limestone

Low pH Cement

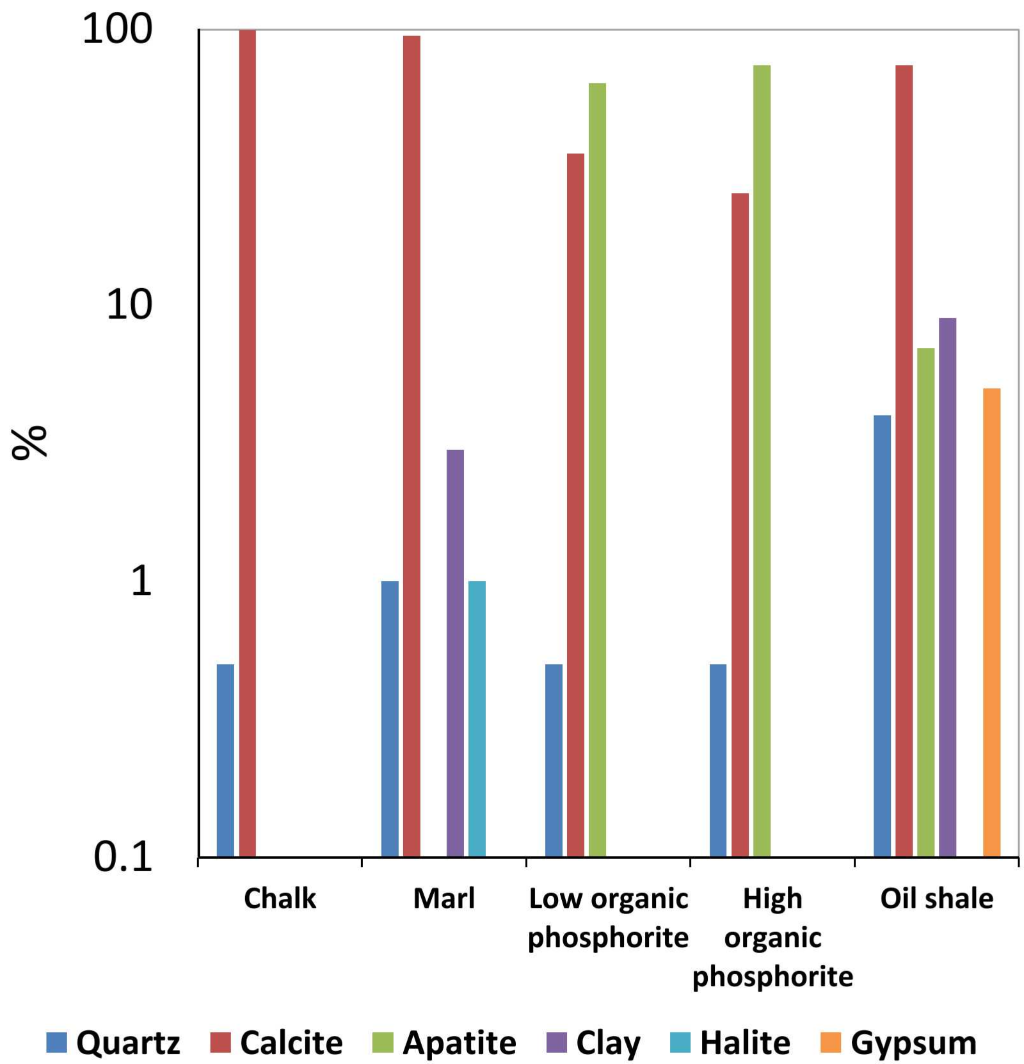
Oil Shale

High OM Phosphorite



Low OM Phosphorite

Rock Mineralogical Composition



Rock	Porosity (%)
Limestone	7
Marl	32
Low organic phosphorite	35
High organic phosphorite	33

Experimental Approach

Batch extraction
Pore water (approx.)
pH dependent leaching (EPA 1313)

→

L/S partitioning
Available content
Mineral set calibration

Monolith diffusion (EPA 1315)
Rock(6) – DI water with LiBr
Cement(2) – DI water

→

Constituent flux
Tortuosity

Rock – Cement Interface
Diffusion tube experiments

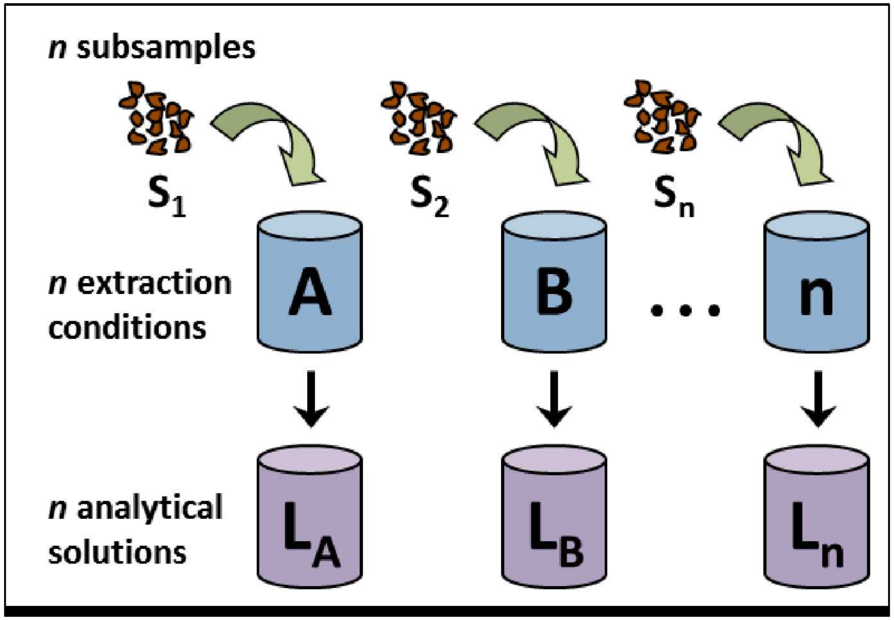
→

Solid phase alteration
Constituent redistribution

Experimental Methods

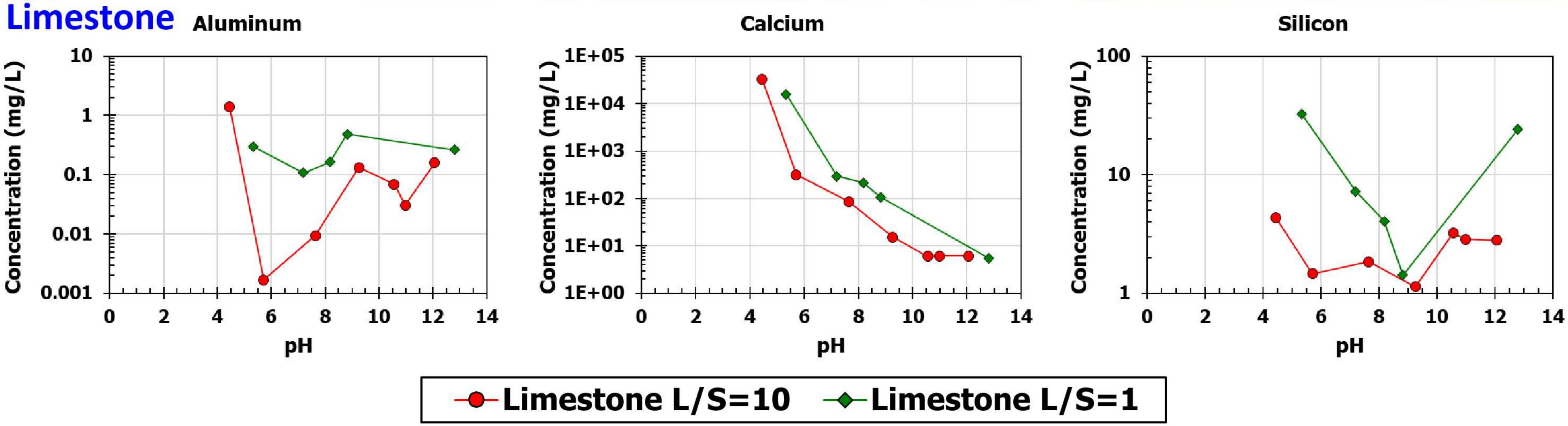
EPA Method 1313

- **pH dependent leaching test**
  - L/S of 10 completed for rock samples and two cement types.
  - L/S = 1 in progress.
- **Analysis**
  - Extracts analyzed using ICP-OES, ICP-MS, TOC, and IC. Additional measurements include pH, conductivity.

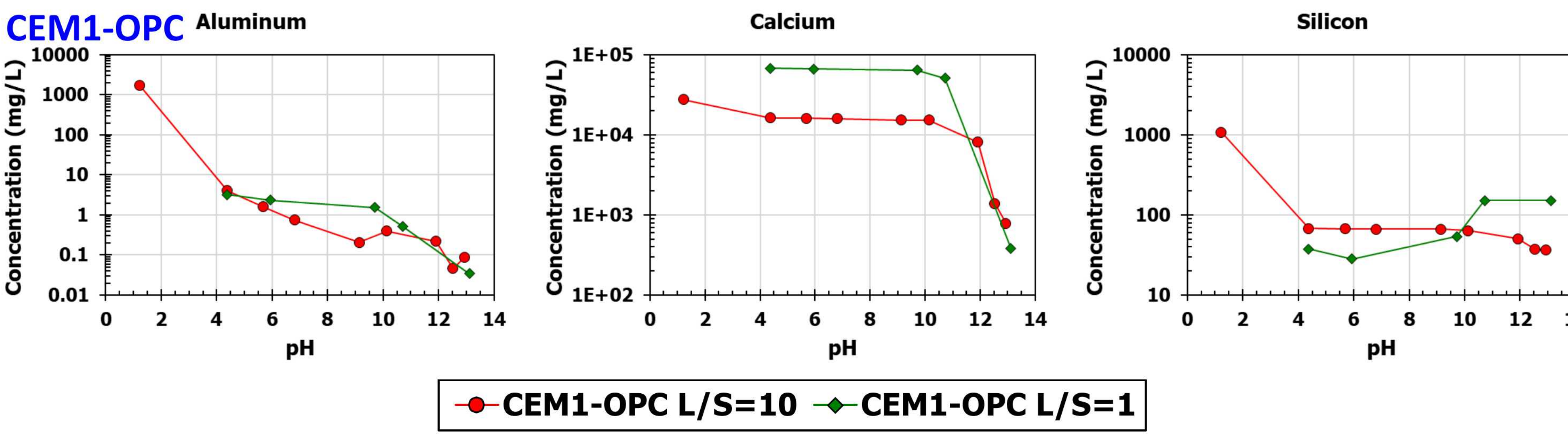


Cement & Rock Results – pH dependent leaching (EPA – 1313)

Limestone



CEM1-OPC

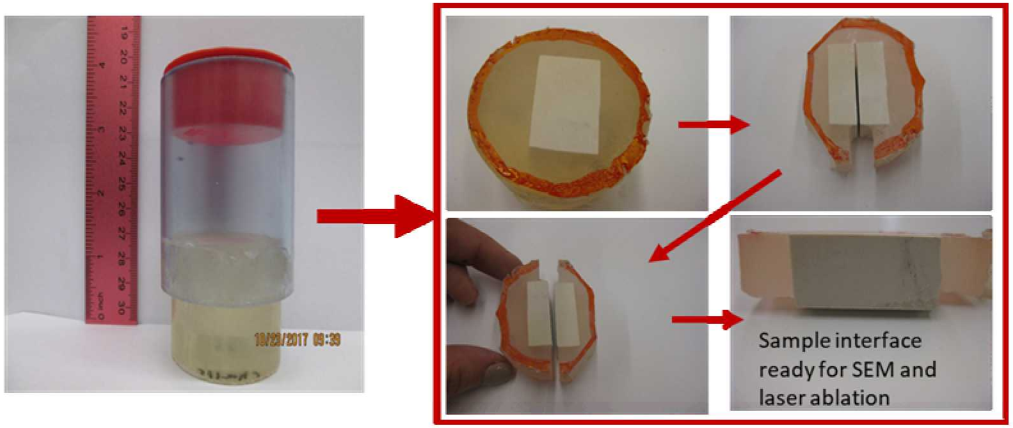


L/S=1 mg/L used to calibrate for trace mineral phases that may completely dissolve at L/S=10 mg/L

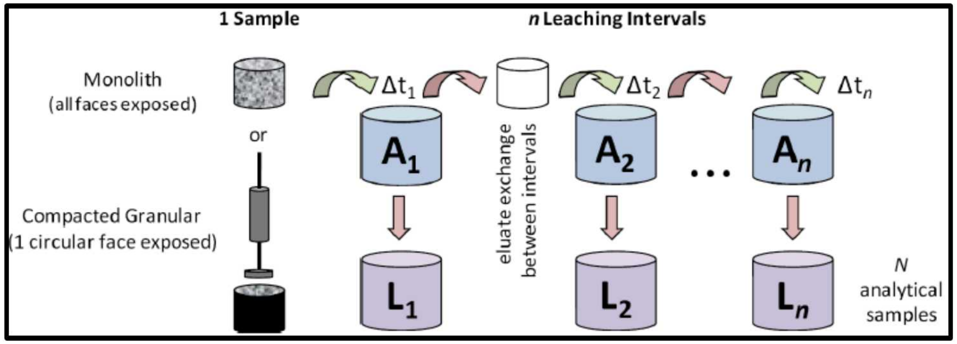
Experimental Methods (EPA 1315)

Method 1315

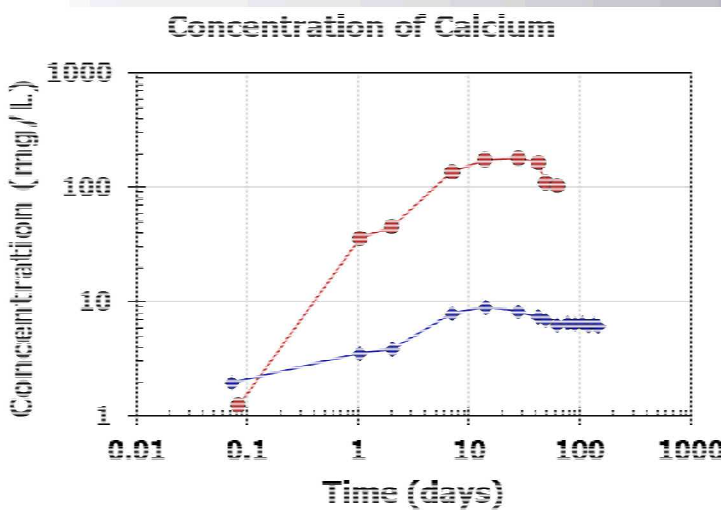
- Mass transfer rate tank leaching test - modified for post-test profile characterization

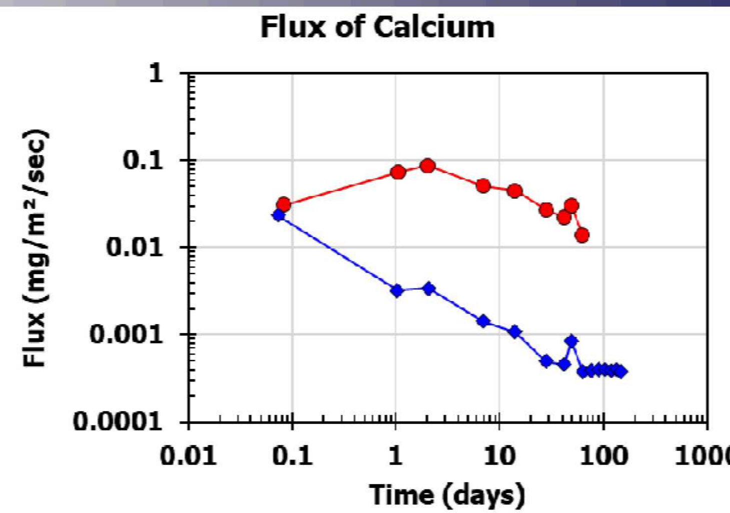


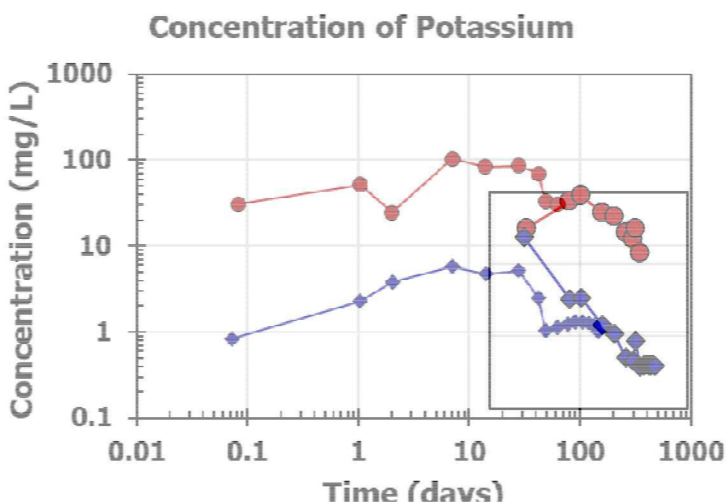
Method 1315 – Experimental set up and sample processing

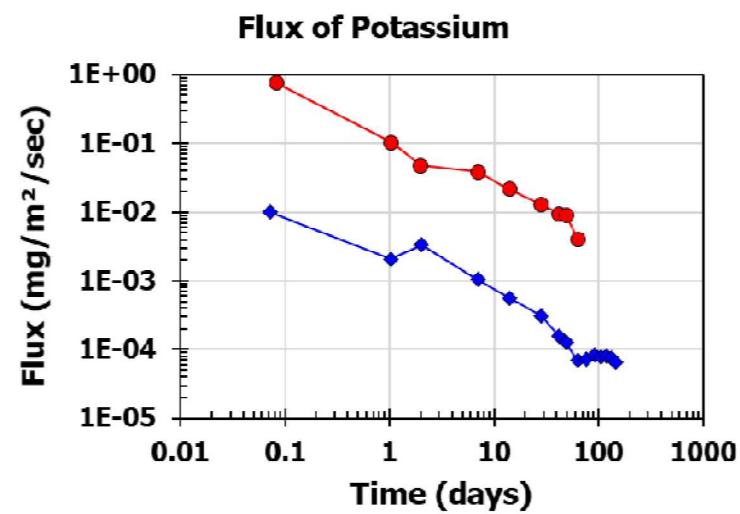


Results – Tank leaching test (EPA – 1315)









CEM1-OPC(M,1,1) Limestone(M,1,1)

Simulation Models and Validation

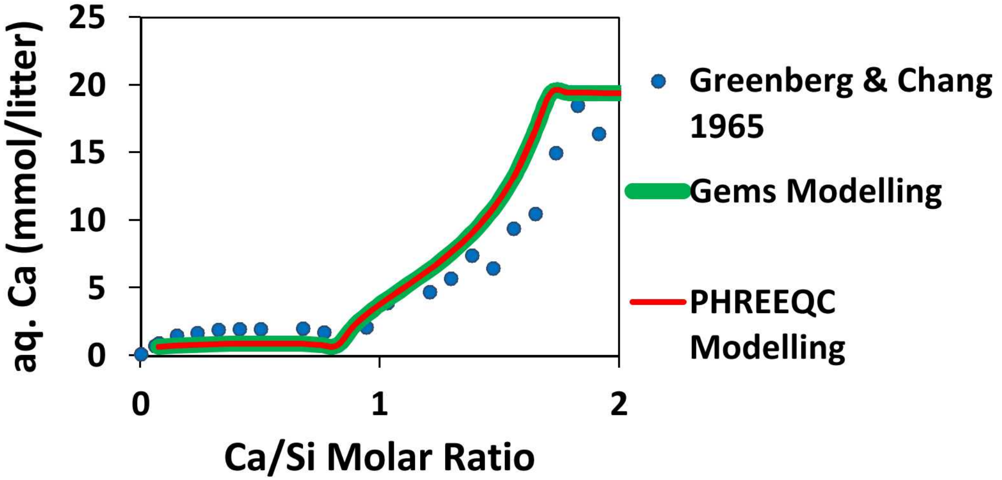
Simulation Models:

- **PFLOTRAN** (3-D, finite element) – Field-scale simulations
- **LeachXS-Orchestra** (1-D, finite volume) – Parameter estimation, analysis of laboratory results
- **Gems** – verification of cement thermodynamics
- **PHREEEQC** – model-to-model verification

CSH Modelling by PHREEQC and Gems:

CSH phases thermodynamic modelling can done using PHRREEQC and Gems which based on different solving methods:

- PHREEQC – Mass action method
- Gems – Gibbs energy minimization method

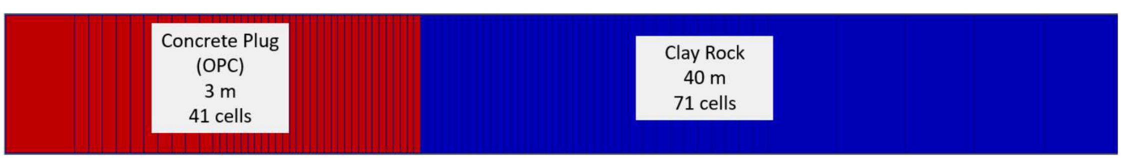


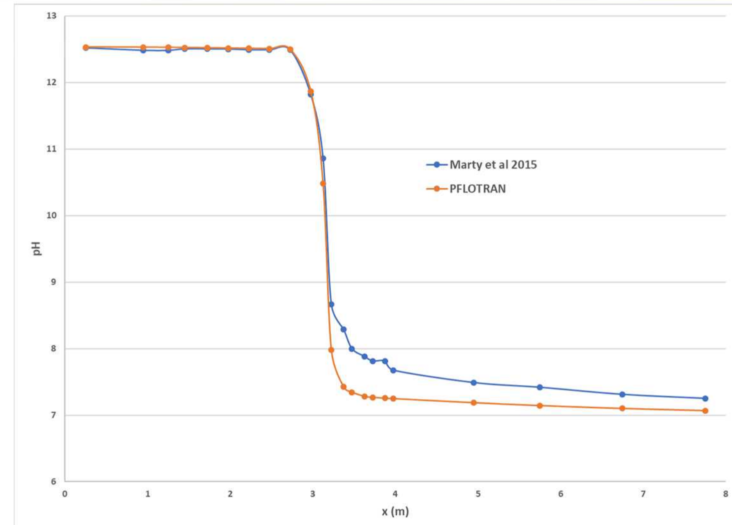
CSH model from Kulik & Kersten 2001

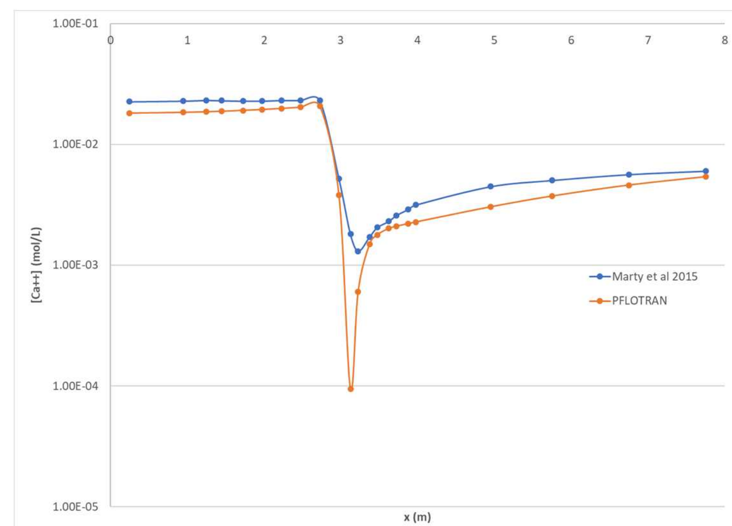
Benchmarking Study

cement / clay rock interface:

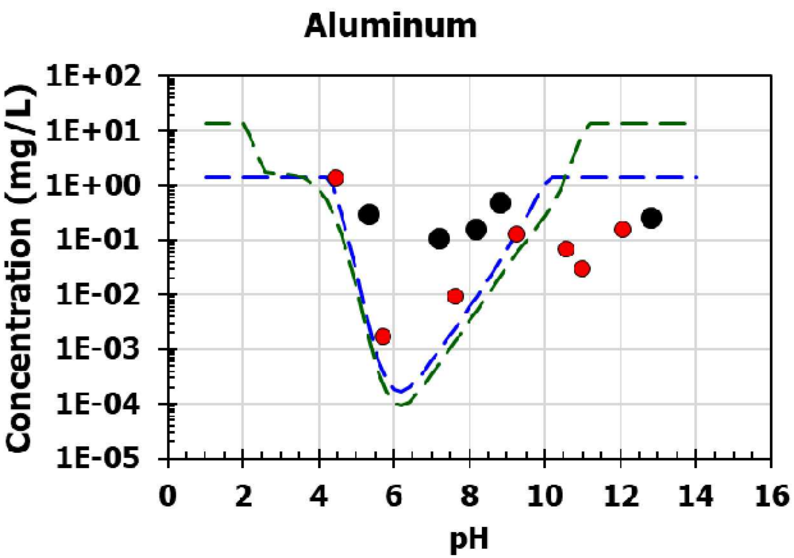
- Benchmarking with **TOUGHREACT**, **PHREEQC**, **CRUNCH**, **HYTEC**, **ORCHESTRA**, and **MIN3P** (Marty et al., 2015)
- 1D **PFLOTRAN** model 25°C and saturated conditions
- A period of 10,000 years was simulated
- 3 meters of OPC plug and 40 meters argillite clay rock

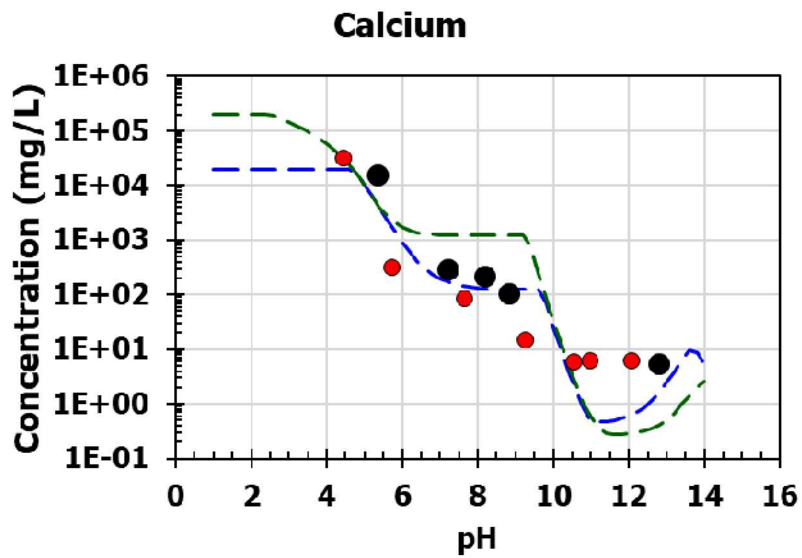


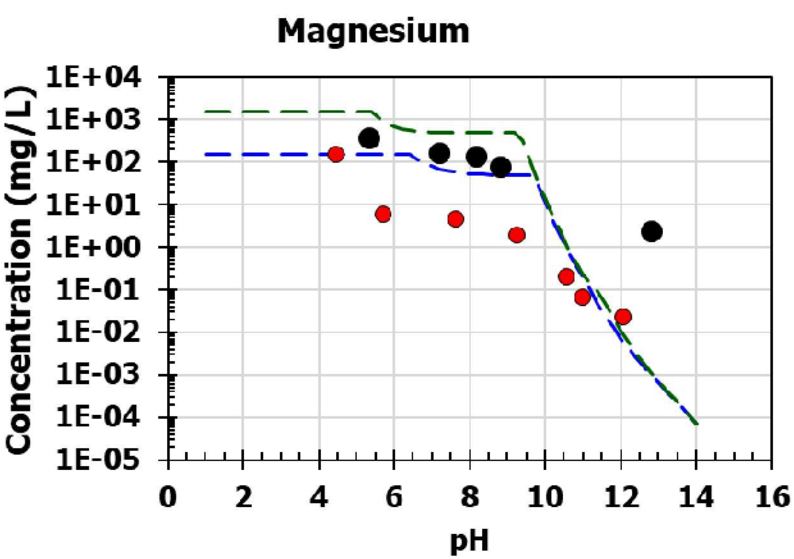




Mineral Set Calibration - Limestone







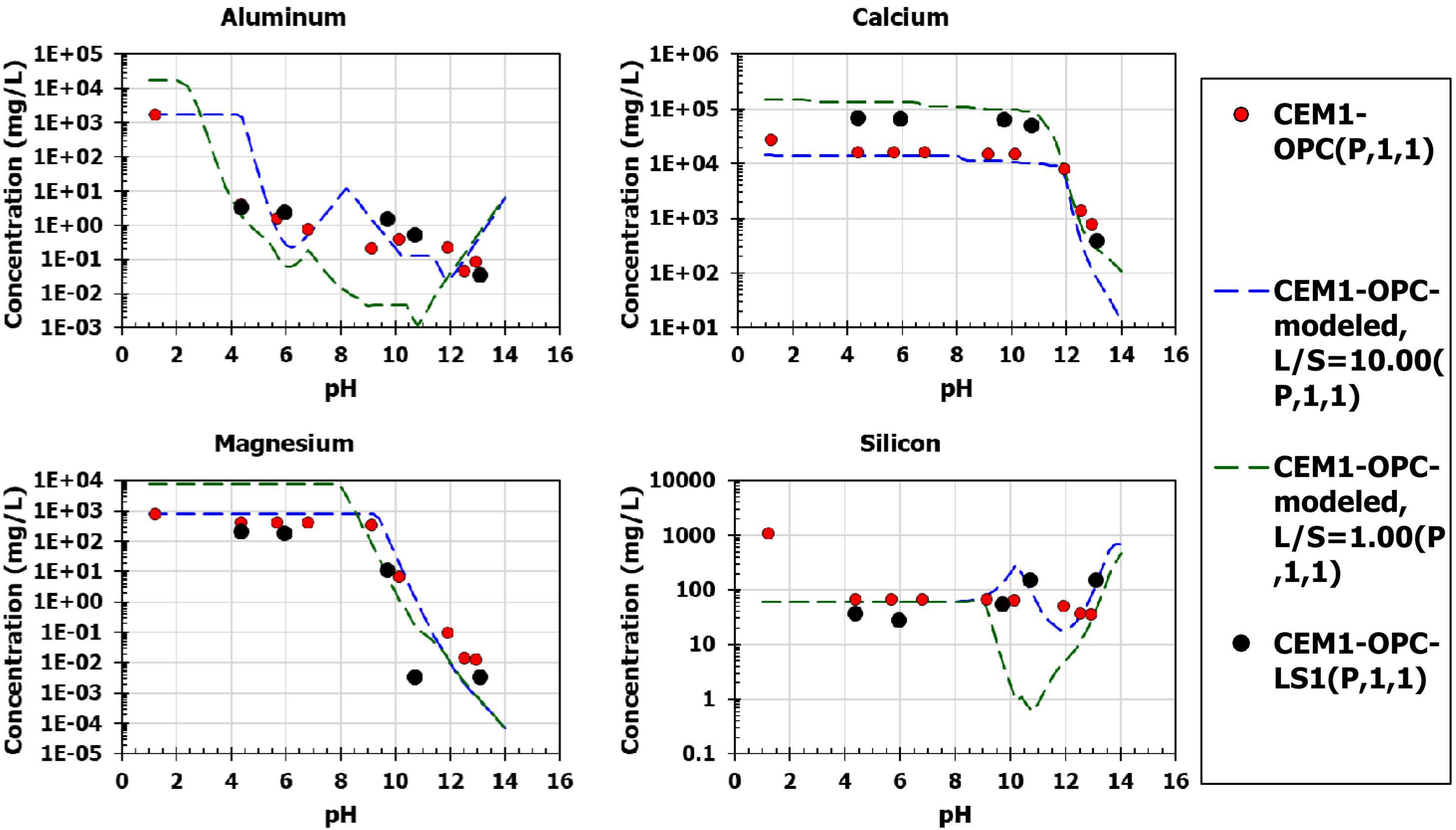
Limestone, L/S=10

Limestone, L/S=1

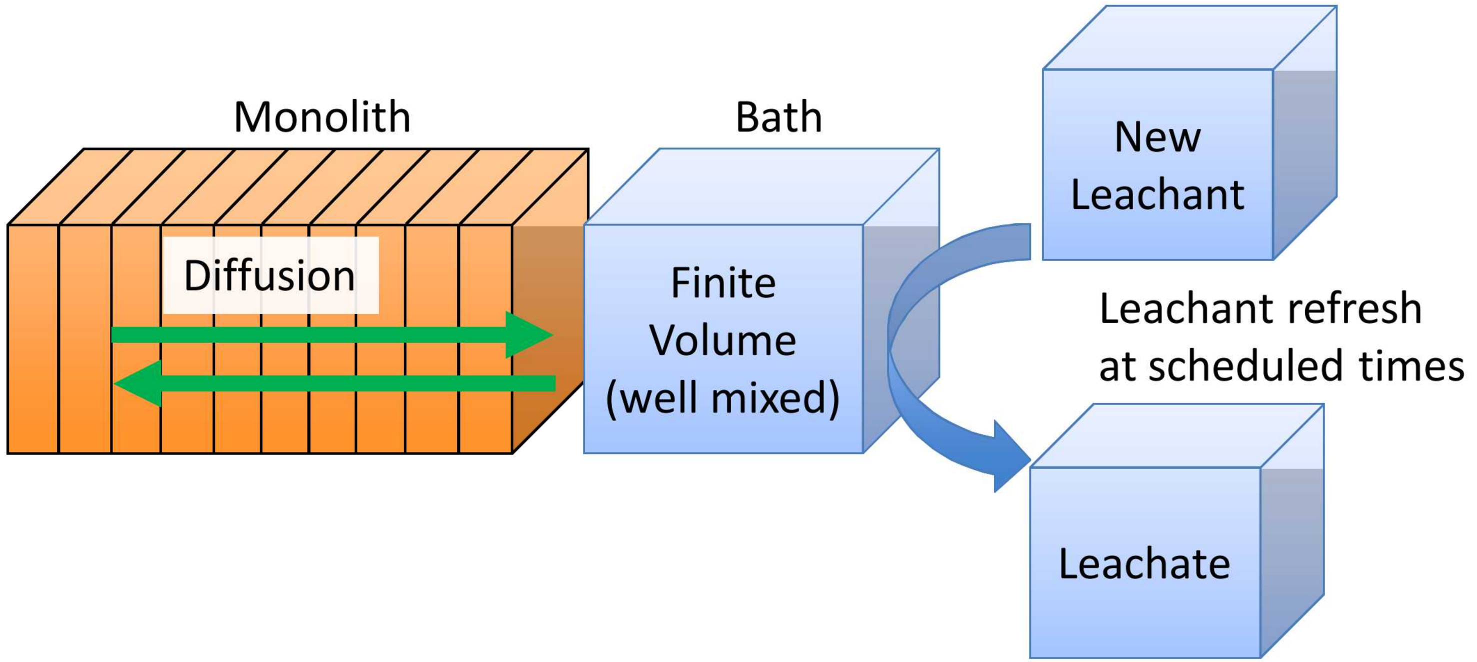
Limestone-modeled, L/S=10.00(P,1,1)

Limestone-modeled, L/S=1.00(P,1,1)

Mineral Set Calibration – CEM1



Dependency of Constituent Flux on Tortuosity



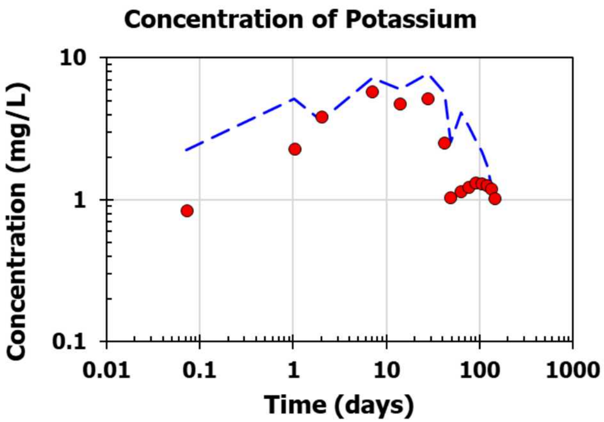
Simulation conditions:

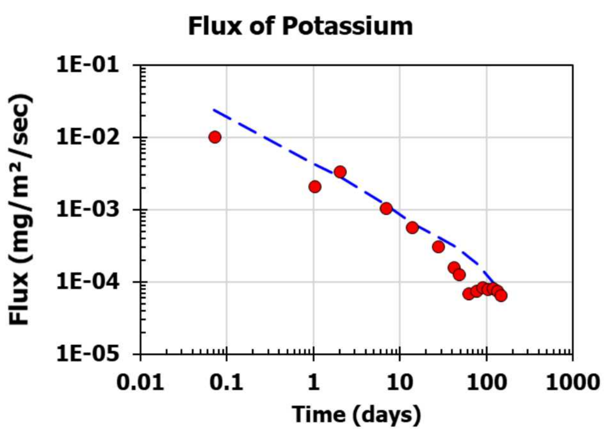
- 133 days simulated to represent 1315 tests duration
- Saturated conditions with measured porosity
- No fluxes at boundaries – diffusion only (multi-ionic diffusion)
- 1-D, 30 cells, each cell is well mixed
- Actual dimensions of monoliths

Tortuosity Calibration – Limestone

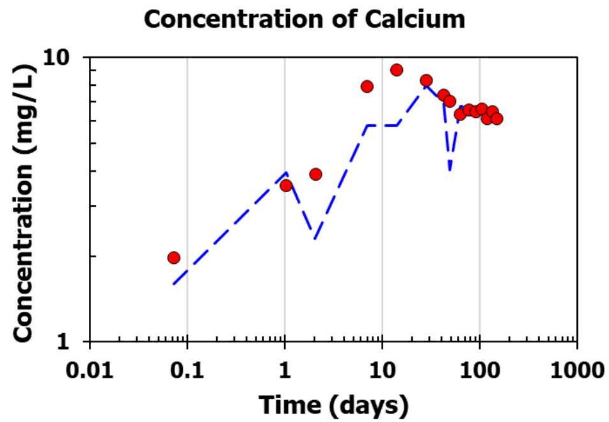
Validation of mineral reaction set calibration (prediction of 1315 test chemistry based on mineral reaction set calibrated by 1313 test)

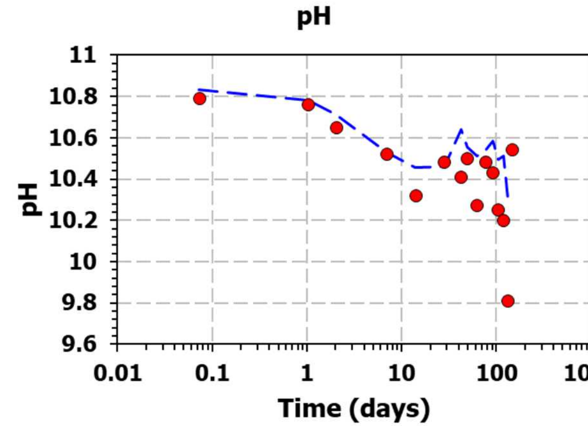
calibration

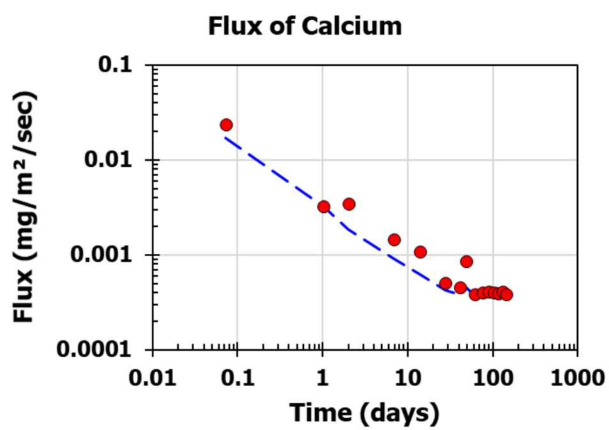


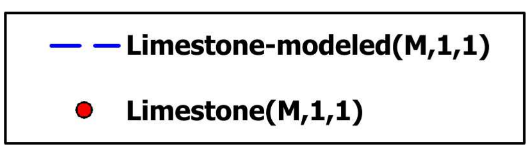


Validation







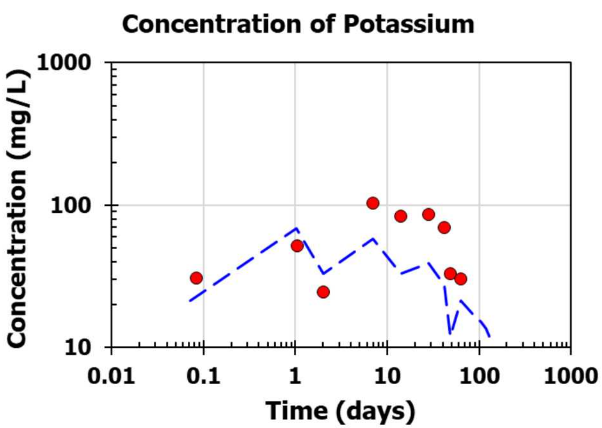


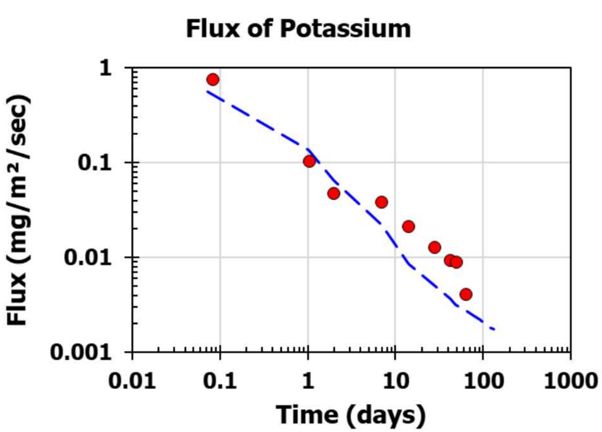
$$\frac{porosity}{tortuosity} = \frac{\emptyset}{\tau^2} = 0.0007$$

Tortuosity Calibration – CEM1

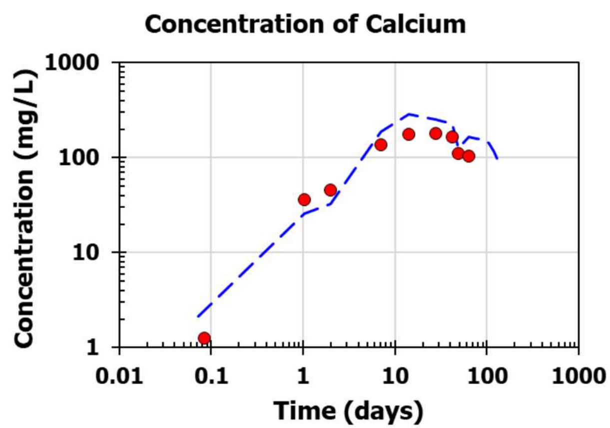
Validation of mineral reaction set calibration (prediction of 1315 test chemistry based on mineral reaction set calibrated in 1313 test)

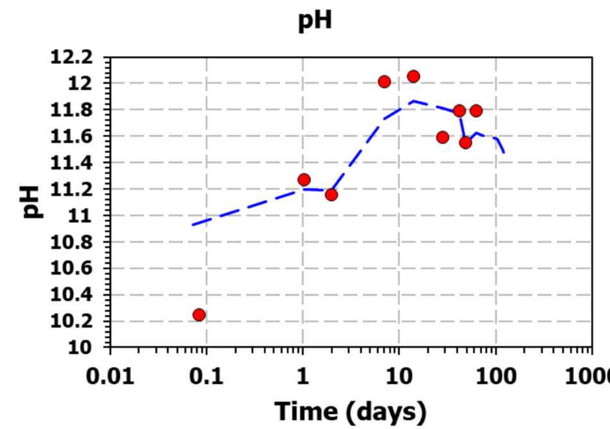
calibration

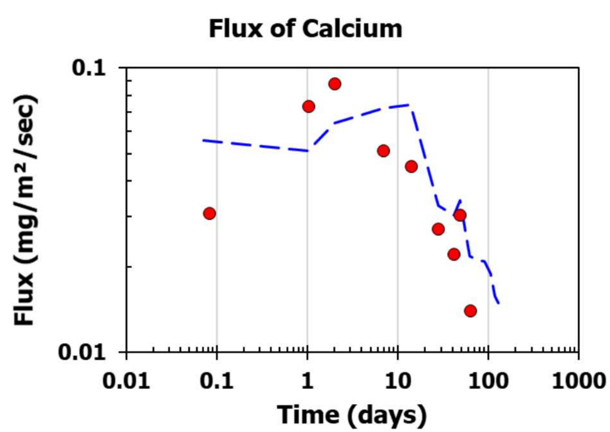


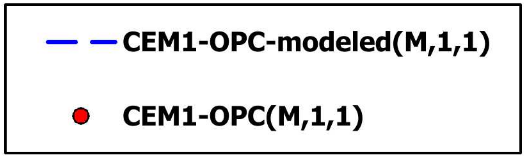


Validation



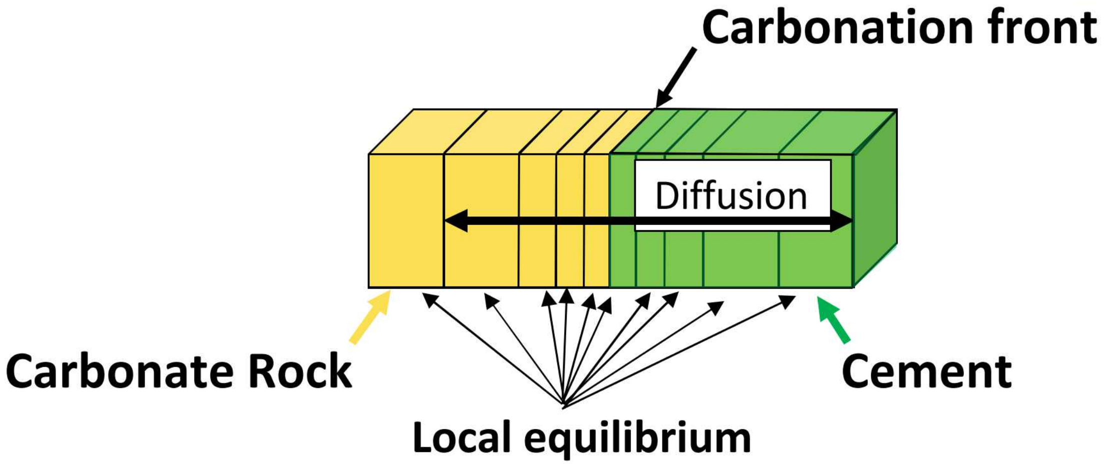






$$\frac{porosity}{tortuosity} = \frac{\emptyset}{\tau^2} = 0.0002$$

Conceptual Model – Rock/Cement Interface



Model assumptions:

1. Each cell is well mixed
2. Local equilibrium
3. C-S-H ideal solid solutions with Tobermorite and Jennite-like end-members
4. Multi-ionic diffusion only

Model conditions for experimental case:

- 5 years simulated, saturated conditions, 30 C
- 1-D, 120 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

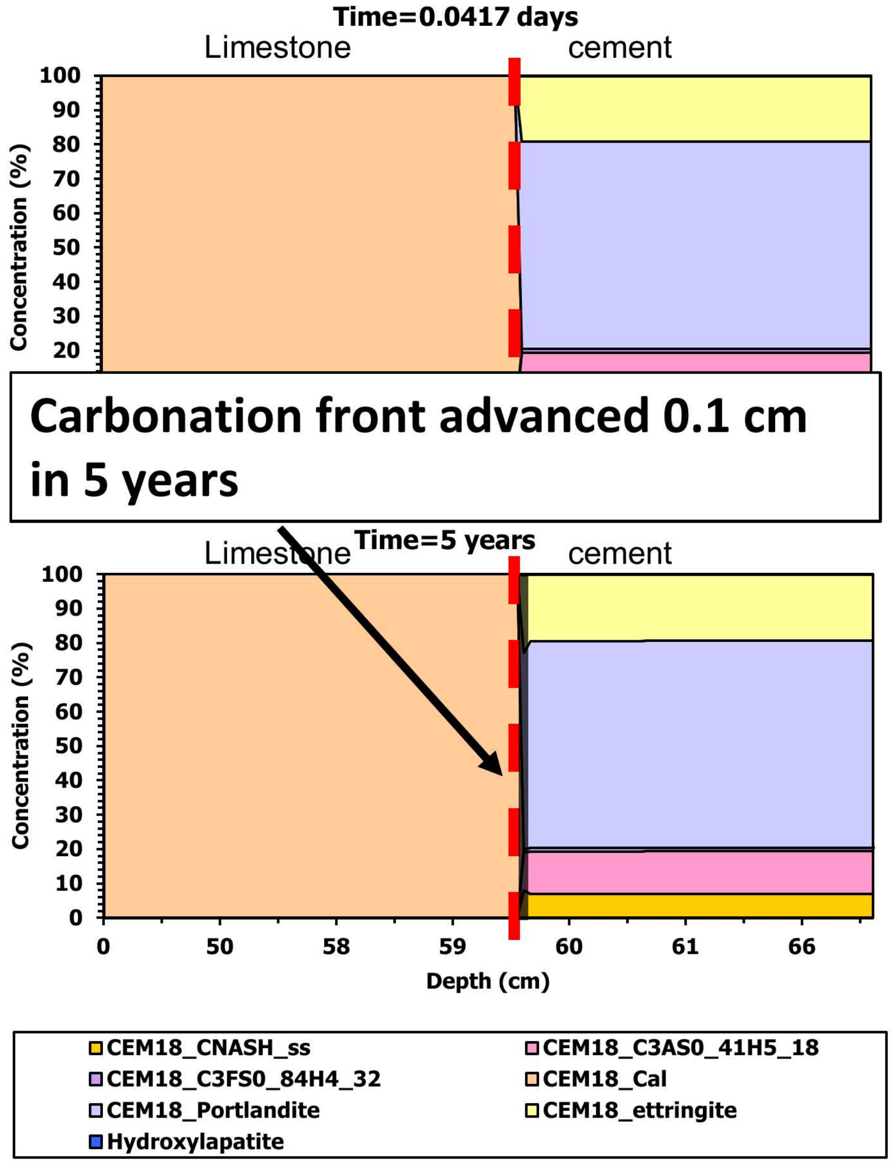
Interface Models

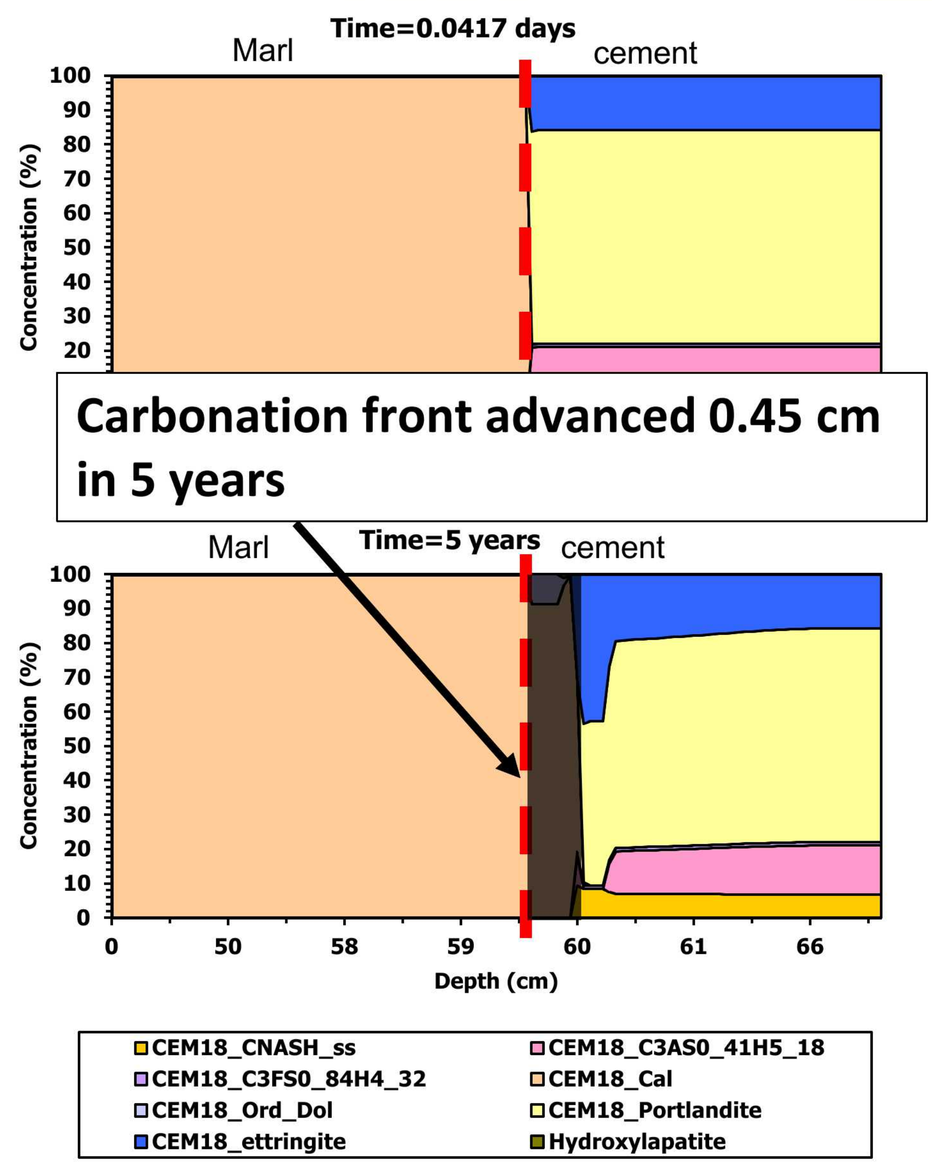
Two interfaces were simulated:

1. Marl – OPC
2. Limestone – OPC

	Limestone	Marl	OPC
Tortuosity (m m^{-1})	10	10	30
Porosity (%)	7	32	15
pH	7.8	7.7	12.9
Carbonate content	high	high	low

Limestone/OPC vs. Marl/OPC Interface Model Results – carbonation





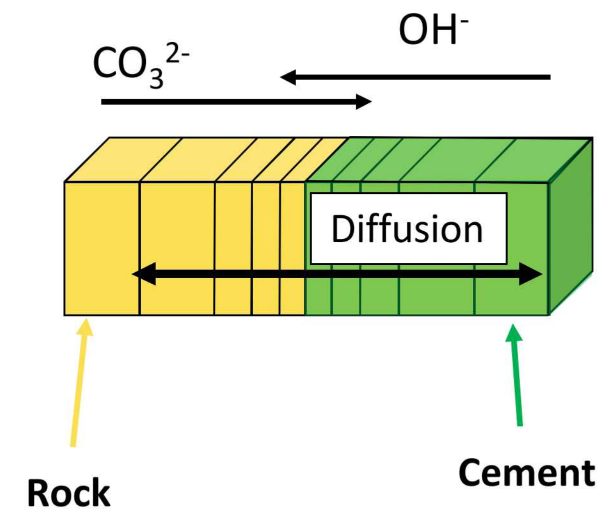
Limestone/OPC vs. Marl/OPC Interface Model Results

Main findings:

- Thicknesses of carbonated cement layer is different for the two interfaces
- The thickness of the carbonated cement layer is controlled by bicarbonate flux from the rock.
- Constituent fluxes are controlled by the ratio of porosity to tortuosity ($\frac{\emptyset}{\tau^2}$).
- ($\frac{\emptyset}{\tau^2}$) is about 4.5 times greater for the Marl than the Limestone – this can account for most of the difference between the rock-cement interface results.

OPC ($\frac{\emptyset}{\tau^2}$) = 0.0002

Interface	Carbonation front progress in 5 years (cm)	Rock ($\frac{\emptyset}{\tau^2}$)
Marl-OPC interface	**0.45**	**0.0032**
Limestone-OPC interface	**0.1**	**0.0007**



Interface Experiments

Current Status:

Cements were cast on **<u>saturated</u>** 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 results:

<u>Approximate times</u>

First sampling - February 2020 (?)

Second sampling - May 2020

Third sampling - November 2020

Future directions

Experimental

- Sampling interface experiments
- Leaching and interface characterization LA-ICP-MS, SEM EDS, …
- Nano indentation - Changes in material mechanical properties as a result of interface reactions
- Unsaturated reaction, moisture transport and temperature variations should be further evaluated

Simulations

- Calibration of mineral reaction sets for rock samples and low pH cement
- Calibration of tortuosity based on 1315 tests for rock and cement samples
- Completion of current set of interface simulations
- Unsaturated reaction, moisture transport and temperature variations should be further evaluated
- Long-term behavior estimates

Acknowledgments

Rich Teising, Emma Wuerth and Peng Zheng (Vanderbilt University)