



This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.



CEMENTITIOUS MATERIALS AGING IN CARBONATE-ROCK/CEMENT-PASTE INTERFACES WITH IMPLICATIONS FOR DEEP GEOLOGICAL DISPOSAL SITES

United States: ¹Chen Gruber, ¹David Kosson, ^{1,2}McKalee Steen, ¹Kevin Brown,
¹Rossane Delapp, ¹John Ayers
²Ed Matteo

Israel: ³Gabriela Bar-Nes, ³Ofra Klein-BenDavid

The Netherlands: ⁵Hans Meeussen

¹Vanderbilt University (VU)

²Sandia National Laboratory (SNL)

³Nuclear Research Center, Negev (NRCN)

⁴Ben-Gurion University of the Negev (BGU)

⁵Nuclear Research and Consultancy Group (NRG)

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and 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. SAND2018-12976 A.

Cementitious materials and carbonate rocks

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



<https://goo.gl/images/Nm2P9a>

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

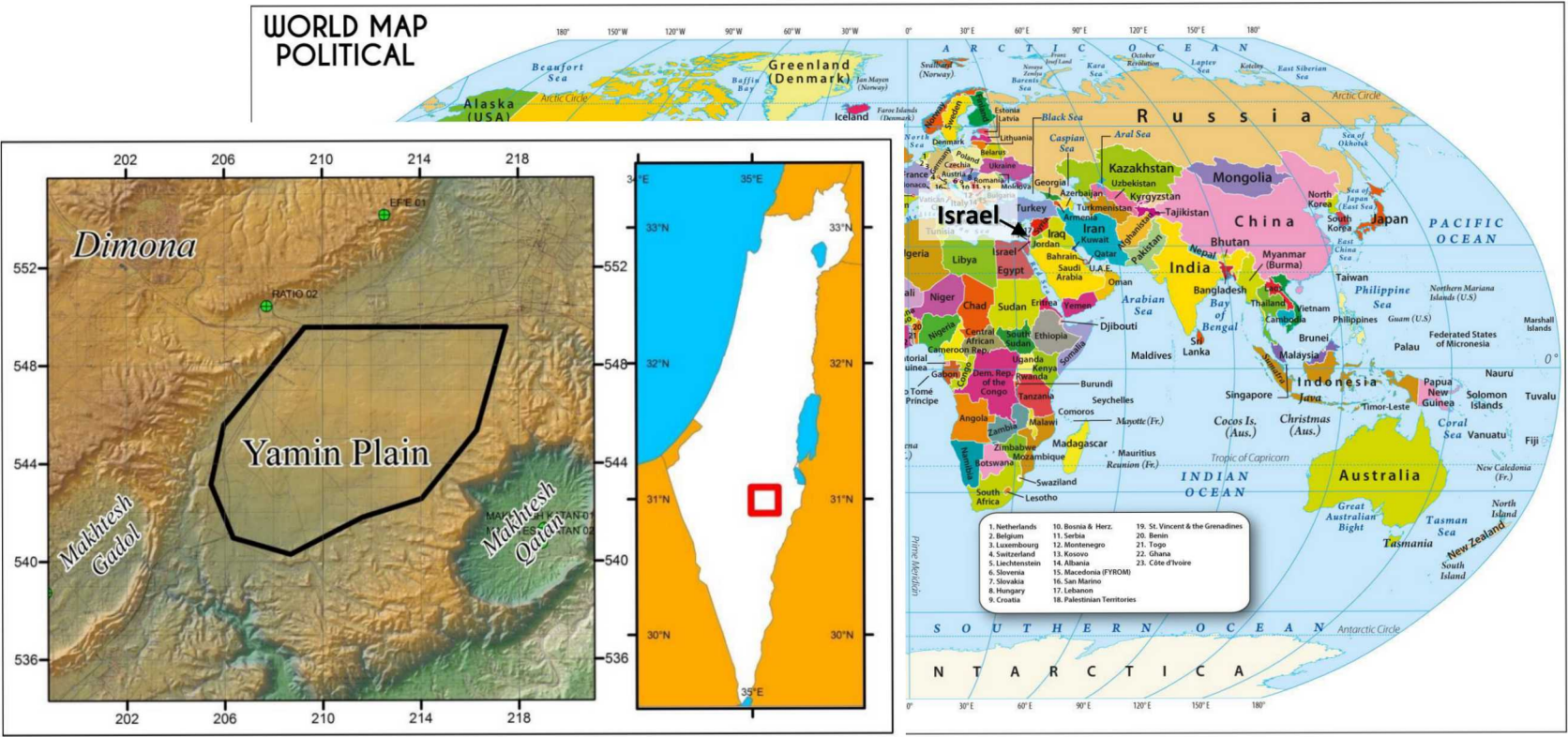
Goal

Characterize the long-term performance of interfaces between cementitious materials (CEM I) with carbonate geologic strata (marl and chalk) of the northern Negev, Israel with respect to primary phases constituents.

Specific objectives:

- i) Use laboratory experiments to characterize the reactions and transport of primary matrix constituents at the interface between carbonate rock types and cementitious barriers.
- 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.

Location map



The location of the study area within the Yamin Plain in the NE Negev (ITM coordinates)

Northern Negev Stratigraphy

STRATIGRAPHY סטרטיגרפיה

SYSTEM תקופה	SERIES - STAGE סדרה / דרגה	SYMBOL סימן	THICK. m עובי מ'	LITHOLOGY מסלע	LITHOSTRATIGRAPHY ליתוסטרטיגרפיה		
					MAPPING UNITS יחידות מיפוי	GROUP חבורה	
QUATERNARY קוורטר	PLEISTOCENE - HOLOCENE פלייסטוקן - הולוקן	Al			Alluvium אלוביום	DEAD SEA ים המלח	
		Qc			Terrace cgl. קונגלומרט טרסות		
TERTIARY טרצייר	NEOGENE ניאוגן	Miocene מיוקן Nh	10 - 40		Gidron Mbr. פרט גדרון	TIBERIAS טבריה	
	Shahaq Mbr. פרט שאחאק				Rotem Mbr. פרט רותם		Hazeva Fm. תצורת חצבה
	PALEOGENE פליאוגן	Eocene איוקן Eav	5 - 70		Undivided Eocene איוקן בלתי מחולק	AVEDAT עבדת	
		Paleocene פליאוקן Th	20		Taqiye Formation תצורת טקיה	MOUNT SCOPUS	
CRETACEOUS קרטיקון	UPPER עליון	Maastrichtian מאסטריוכט Kug	25 - 75		Ghareb Formation • Marl • Oil shale		JUDEA יהודה
		Senonian סנוניאן	Campanian קמפן Kum1		20 - 40		
	LOWER תחתון	Santonian סנטון Kum	0 - 60		Nezer Formation תצורת נצר	JUDEA יהודה	
		Turonian טורון Kush	0 - 40		Shivta Formation תצורת שבטה		
		Kud	0 - 30		Derorim Formation תצורת דרורים		
		Cenomanian קנומן Kut	40 - 80		Tamar Formation תצורת תמר		

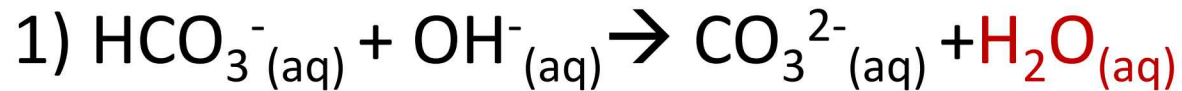
Most of the surface and subsurface rocks in Israel consist of carbonate rocks

Cementitious materials and carbonate rocks

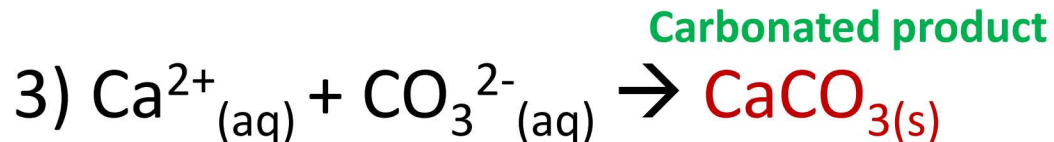
Carbonation process:

- Reaction of aqueous CO_2 with hydration minerals including portlandite, to form carbonated products and water

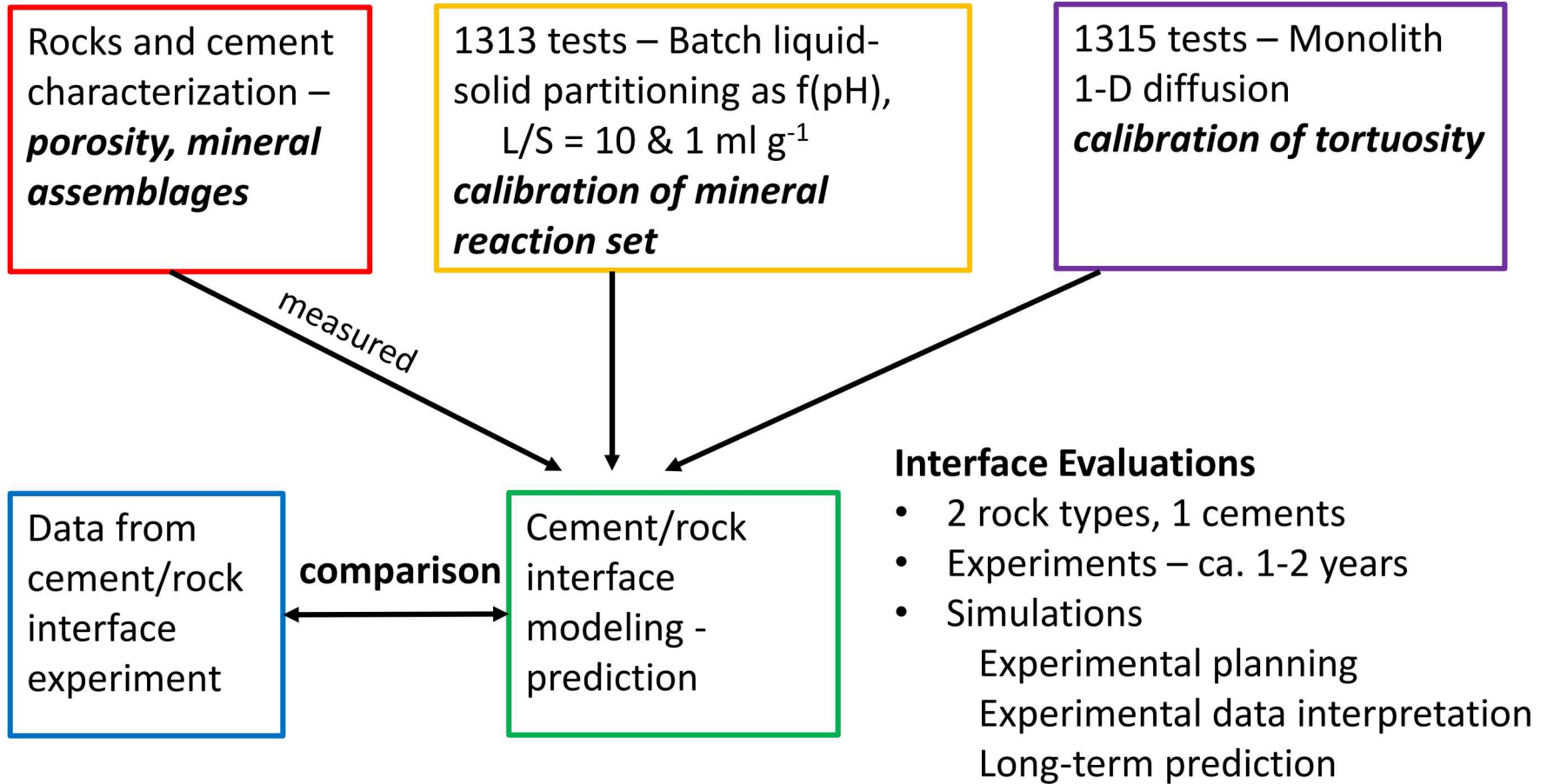
Transformation of bicarbonate to carbonate



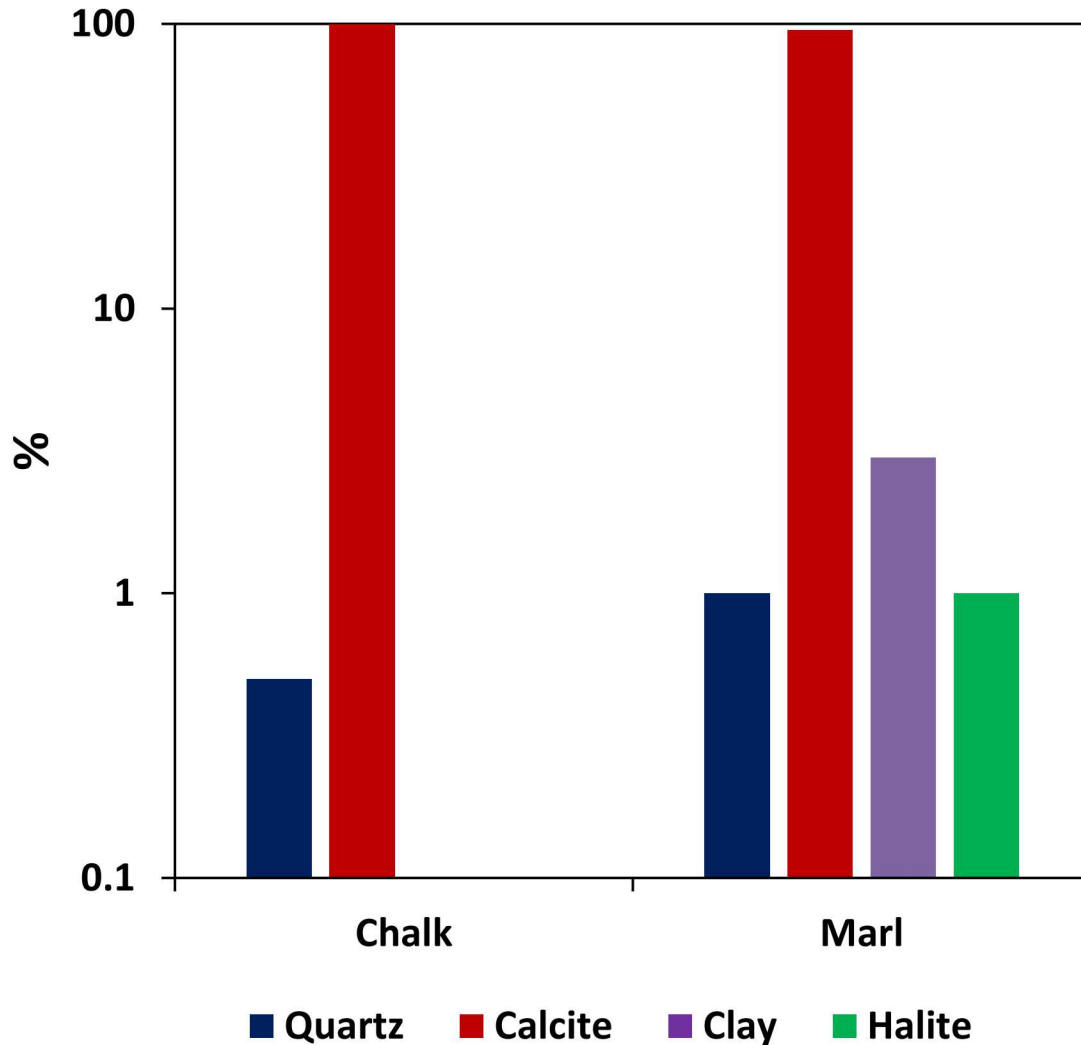
Portlandite



Project approach

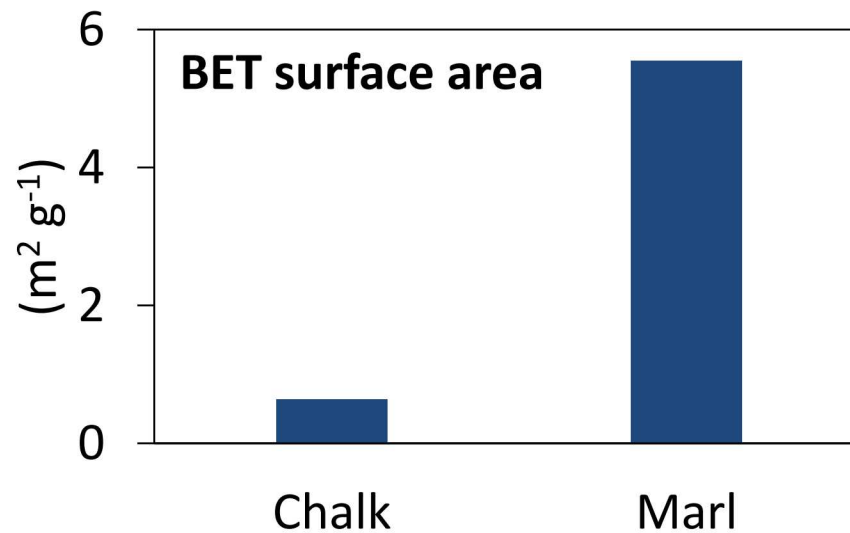
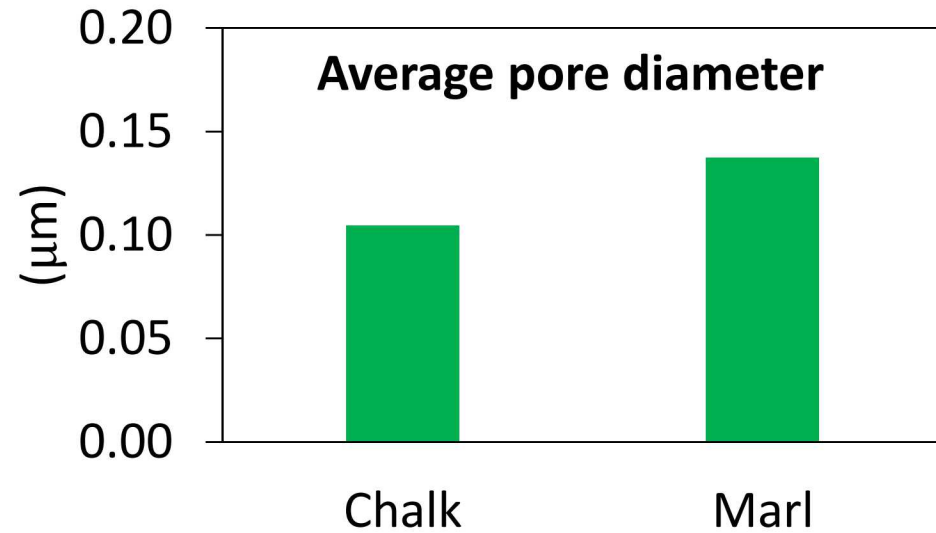
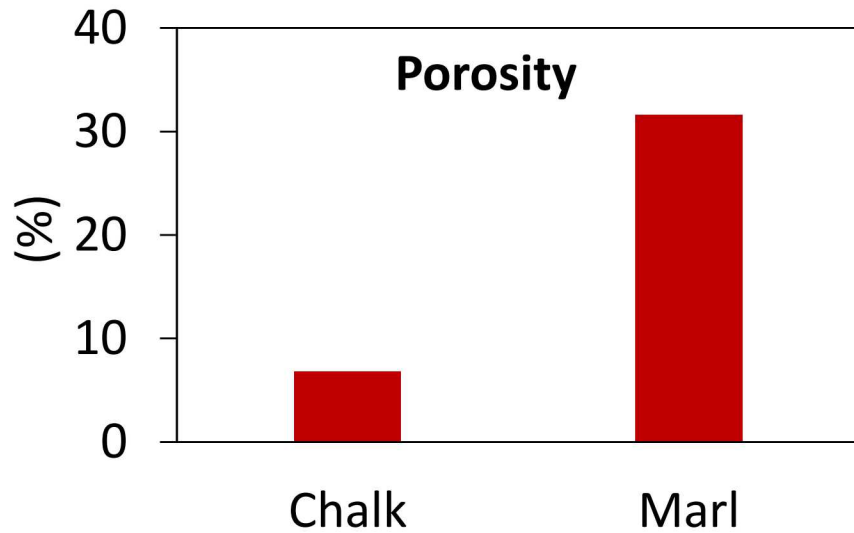


Rock mineralogical composition



- Calcite is dominant to major component in both rocks
- Clay is a minor component in the marl
- Major clay component: illite-smectite (r)

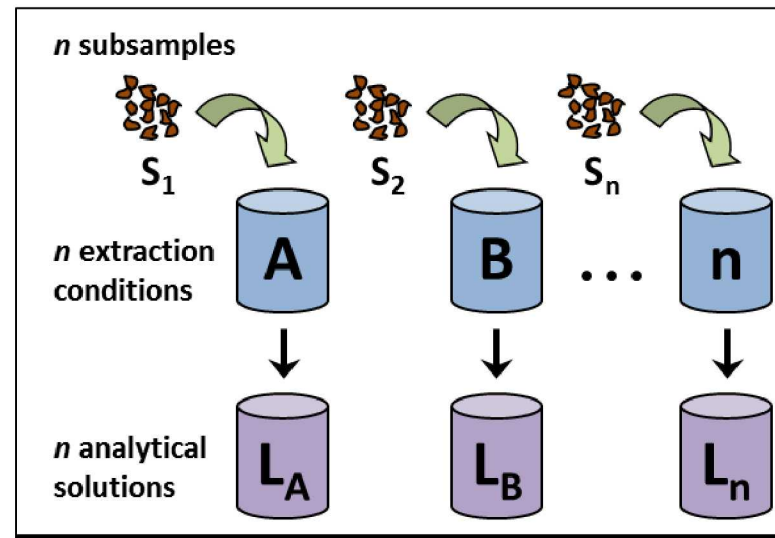
Petrophysical characteristics



Experimental methods (EPA 1313)

Method 1313

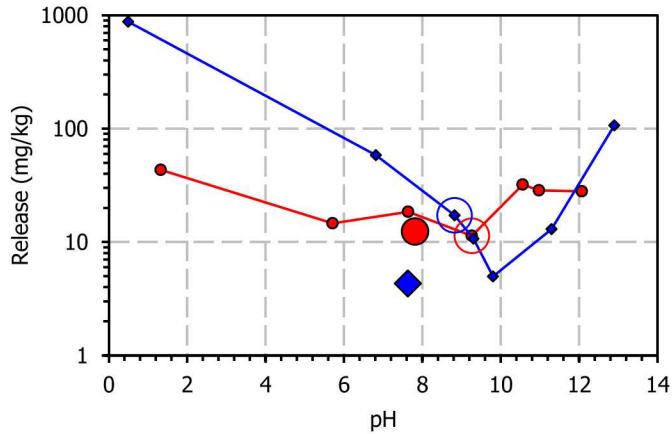
- pH dependent leaching test
 - L/S of 10 ml g⁻¹ completed for rock samples and two cement types.
 - L/S = 1 ml g⁻¹ in progress.
- **Analysis**
 - Extracts analyzed using ICP-OES, ICP-MS, DOC, and IC. Additional measurements include pH, conductivity.



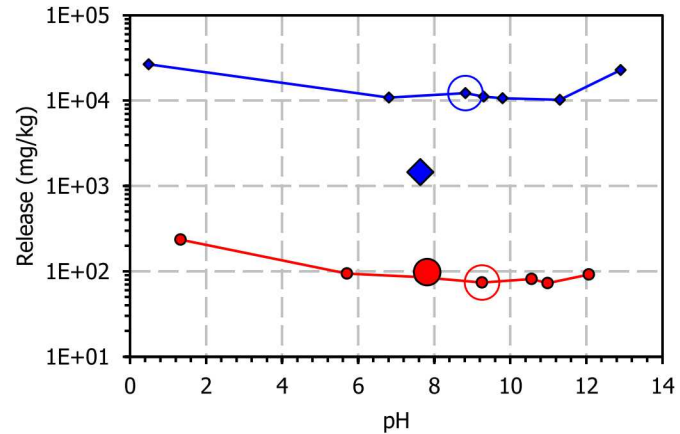
Endpoint pH <2 to 13

Experimental methods (EPA 1313)

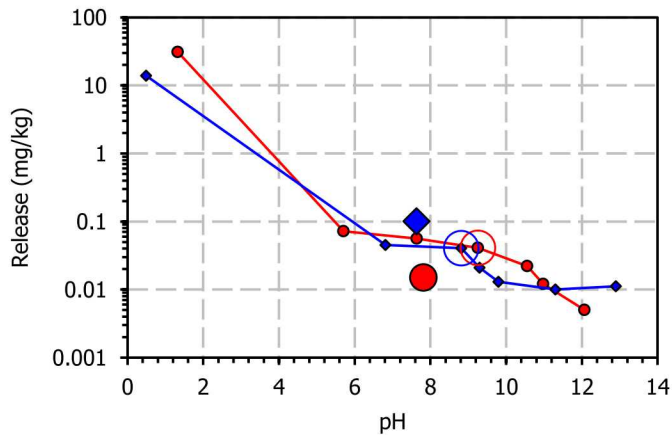
pH dependent release of Silicon



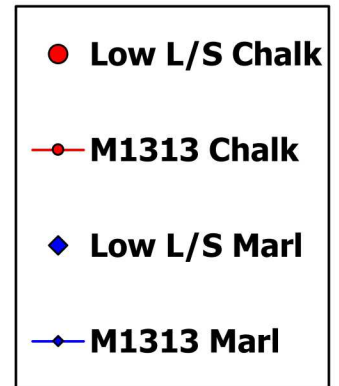
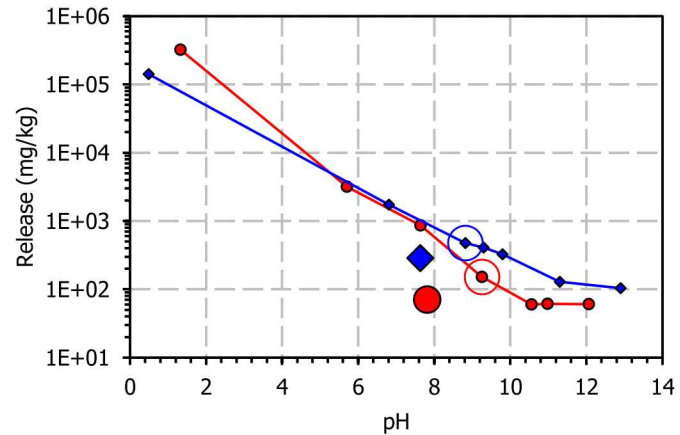
pH dependent release of Sodium



pH dependent release of Lithium

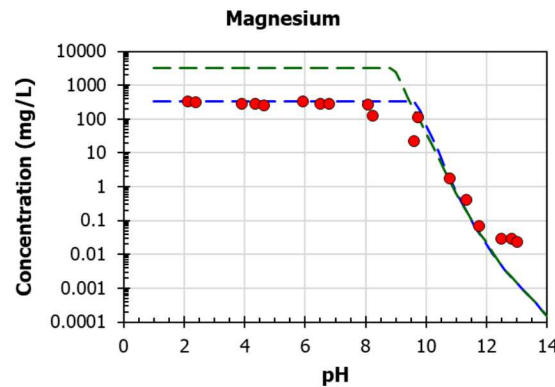
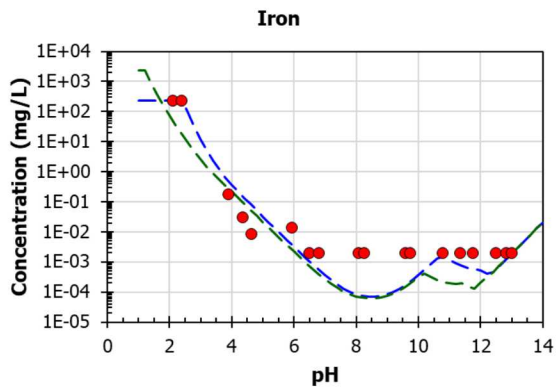
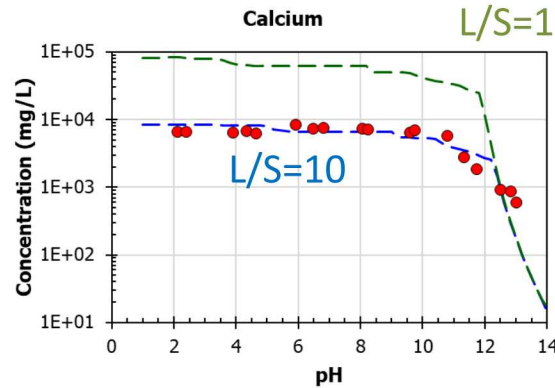
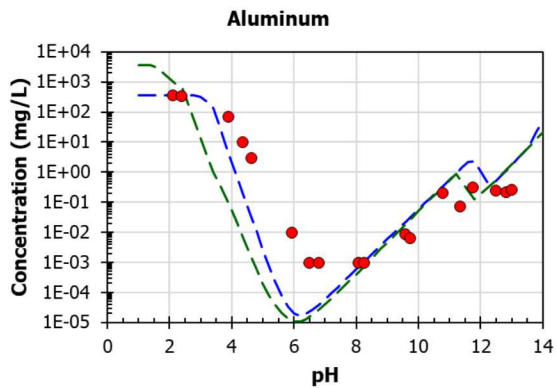


pH dependent release of Calcium



Selection of mineral reaction set

Calibration of reaction set to 1313 tests (illustration only)

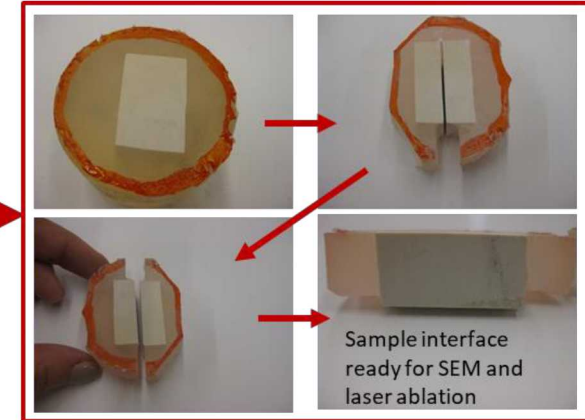


- Need to be calibrated to different L/S ratios
- $L/S=1$ mg/L used to calibrate for trace mineral phases that may completely dissolve at $L/S=10$ mg/L
- Sometimes metastable phases are preferred over the stable phase

Experimental methods (EPA 1315)

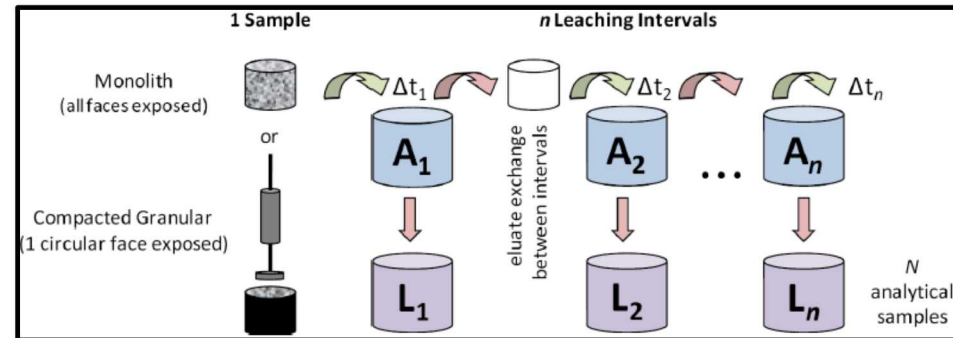
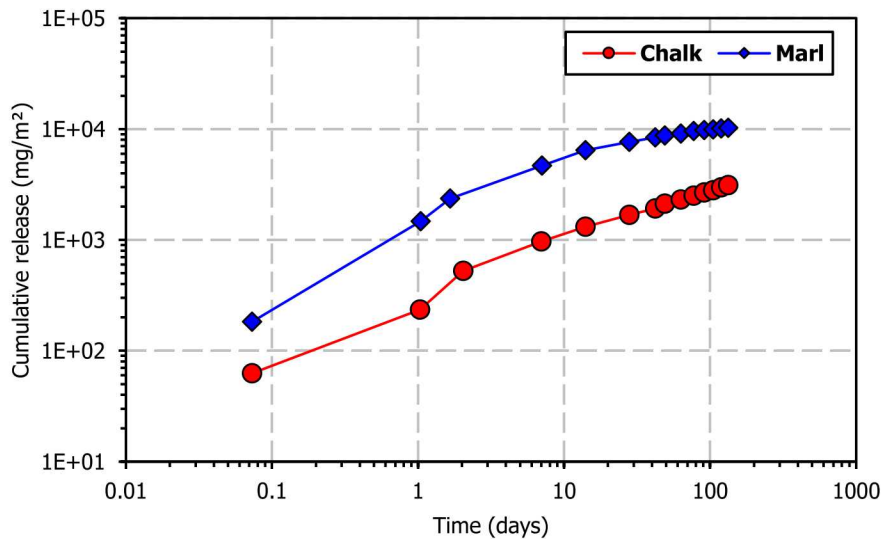
Method 1315

- Mass transfer rate tank leaching test - modified for inclusion of LiBr as ingress tracer & post-test profile characterization



Method 1315 – Experimental set up and sample processing

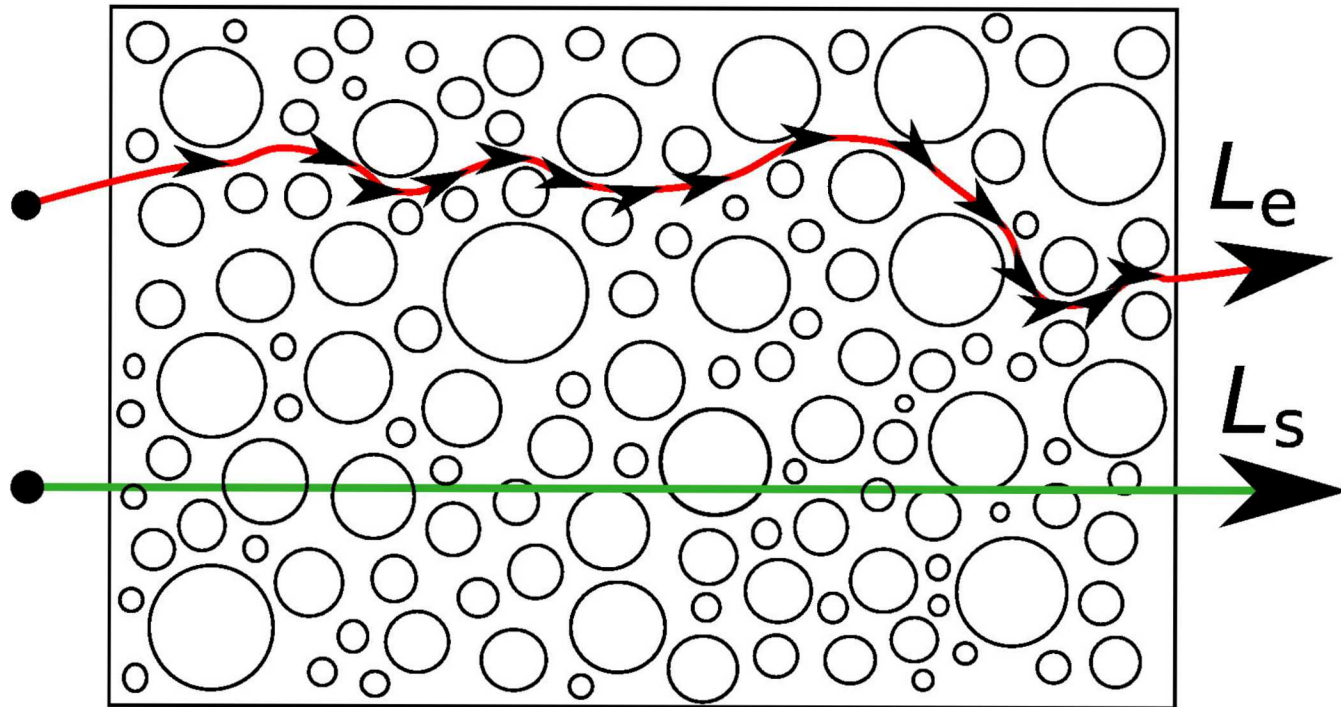
Cumulative release of Potassium



Tortuosity calibration

Tortuosity, τ , is defined as the ratio of the length of the real diffusion path, L_e , to the path in the straight channel case, L_s

$$\tau = \frac{L_e}{L_s}$$

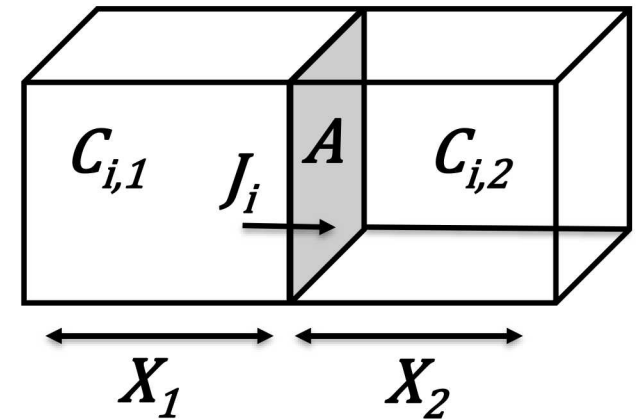


The dependency of constituent flux on Tortuosity

Constituent flux:

$$J_i = -D_i \cdot dC_i \cdot \frac{A \cdot \varphi}{\tau^2}$$

Assume linear relationship between porosity and contact area



J_i - flux (mol s^{-1})

D_i - diffusion coefficient of the i^{th} constituent ($\text{m}^2 \text{s}^{-1}$)

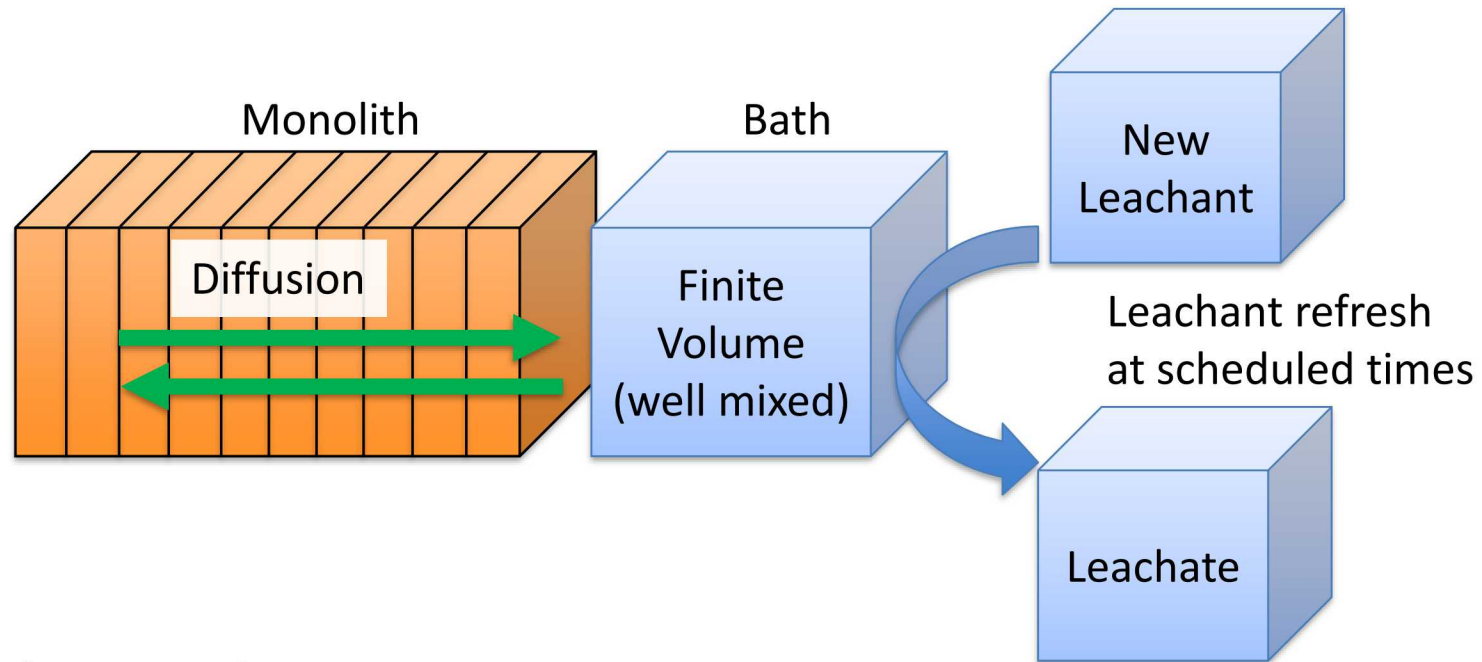
dC_i - concentration gradient (dC/dX) of the i^{th} constituent (mol m^{-2})

A - contact area (m^2)

φ - porosity

τ - tortuosity (m m^{-1})

The dependency of constituent flux on Tortuosity

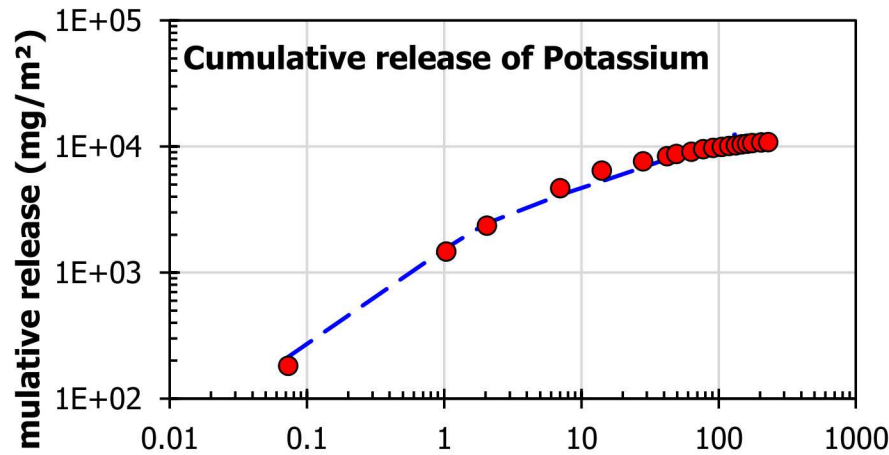


Simulation conditions:

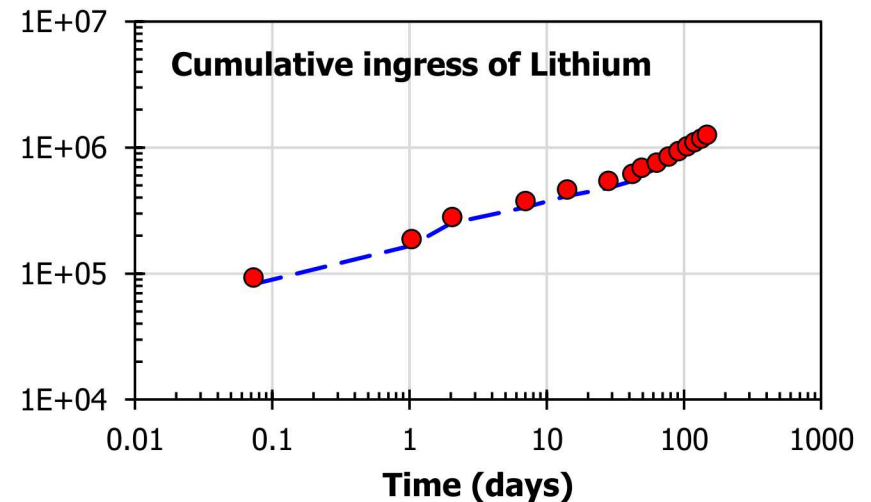
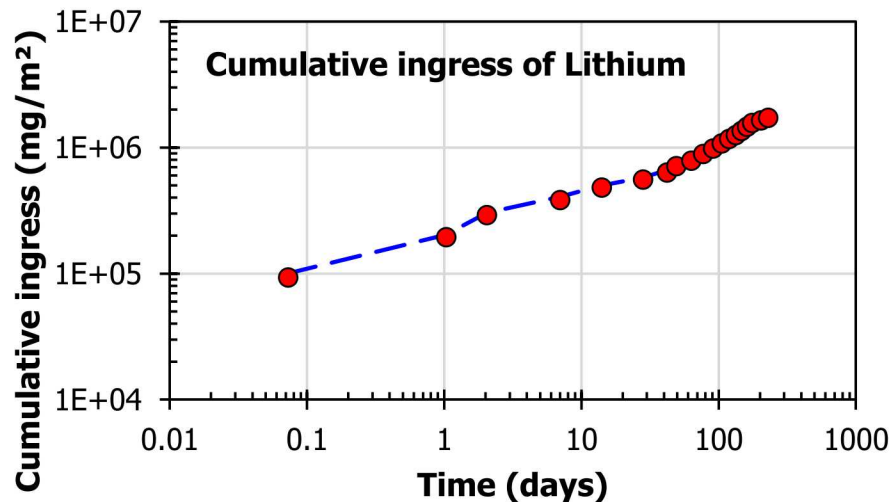
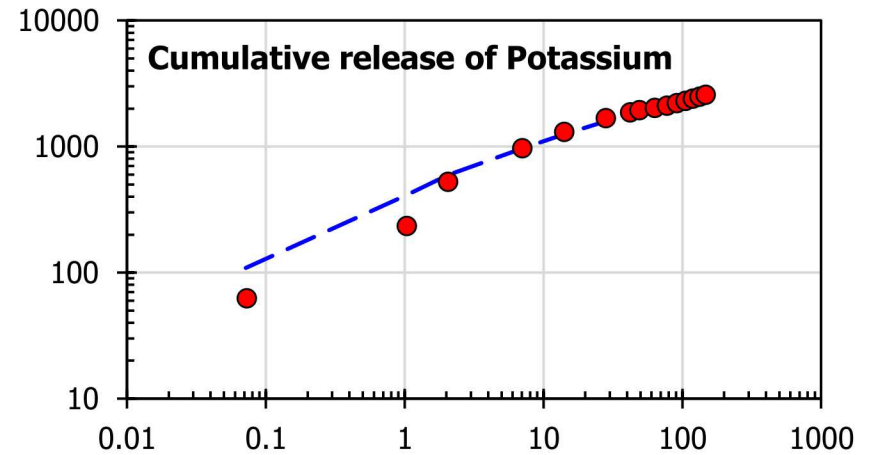
- 133 days simulated to represent 1315 tests duration
- Saturated conditions with measured porosity
- No fluxes at boundaries – diffusion only (multi ionic diffusion)
- 1-D, 30 cells, each cell is well mixed
- Actual dimensions of monoliths

The dependency of constituent flux on Tortuosity

Marl



Chalk



— Model Material(M,1,1) ● Marl(M,1,1)

— Model Material(M,1,1) ● Chalk(M,1,1)

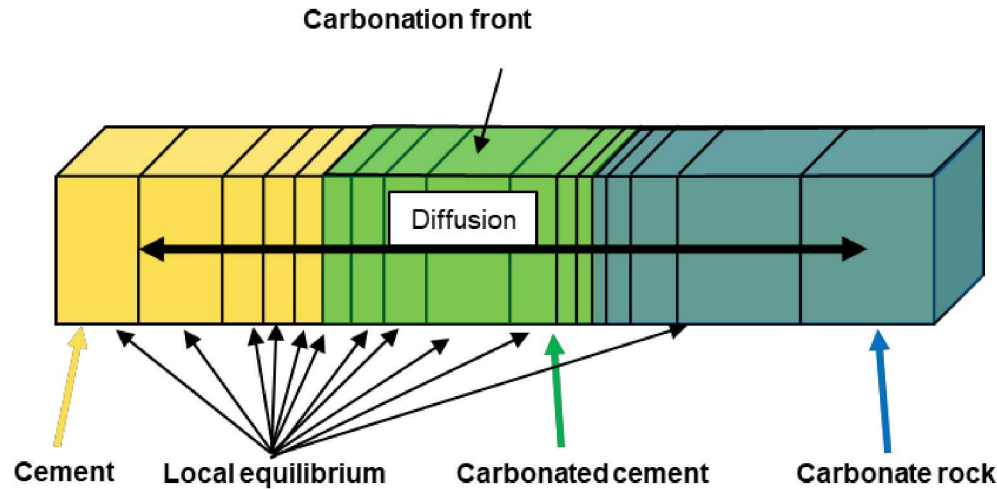
Interface models

Two interfaces were simulated:

1. Marl – OPC
2. Chalk – OPC

	Chalk	Marl	OPC
Tortuosity ($m\ m^{-1}$)	50	87	30
Porosity (%)	6.8	31.7	15.8
pH	7.8	7.7	13.6
Carbonate content	high	high	low

Conceptual model – Laboratory Simulation Cases



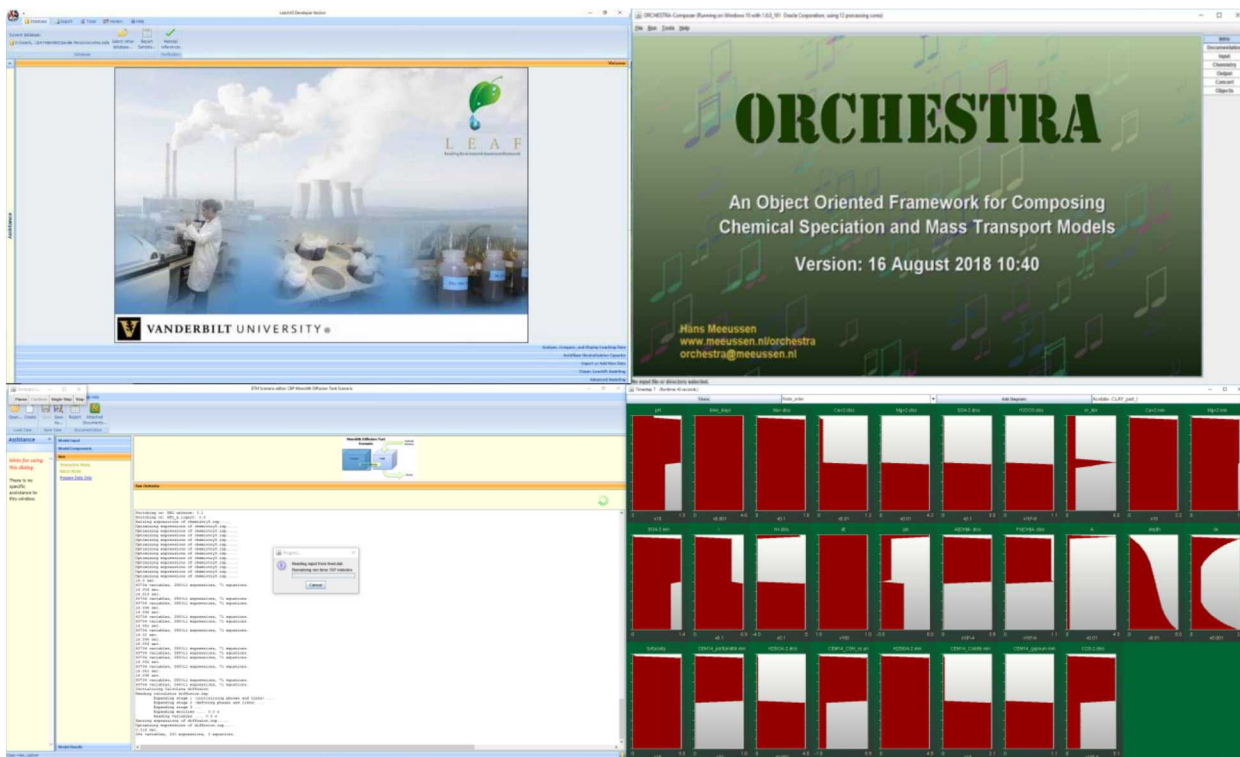
Model assumptions:

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

Model conditions for experimental case:

- 5 years simulated, saturated conditions, 25 C
- 1-D, 120 cells, Finite volume
- No fluxes at boundaries – diffusion only (multi ionic diffusion)
- Thermodynamic database – CEMDATA14 (Lothenbach et al. (2014))

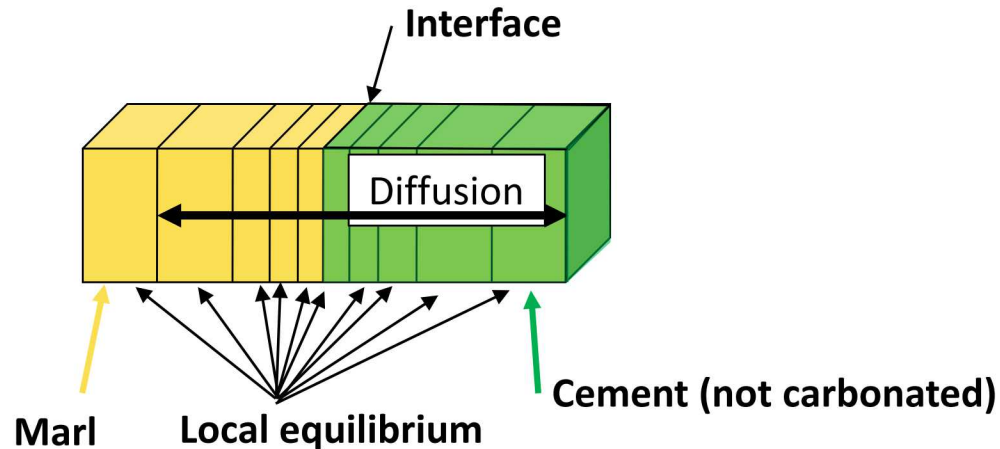
Models in LeachXS™-ORCHESTRA



- Reactive Transport model
- Simulating field or laboratory scenarios
- Flexible interface conditions (e.g., fixed volume, continuous flow or intermittent flow / exchange & solutions)
- Leaching data management integrated with chemical speciation – reactive transport modeling

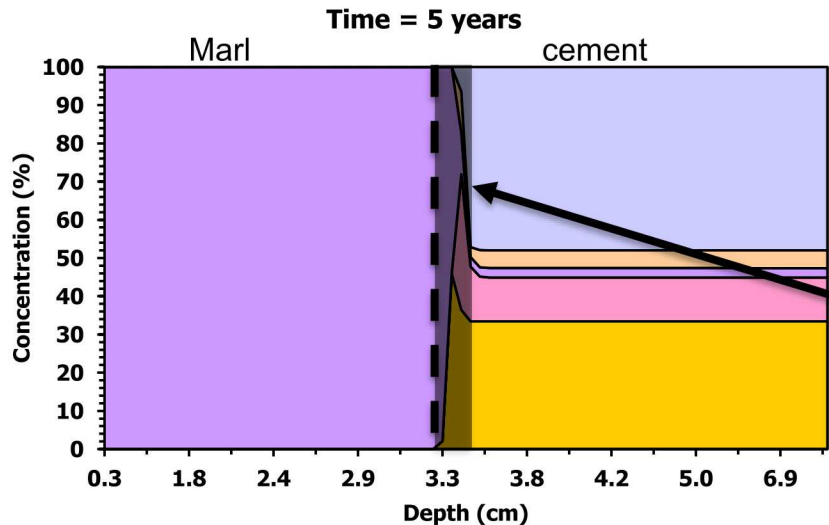
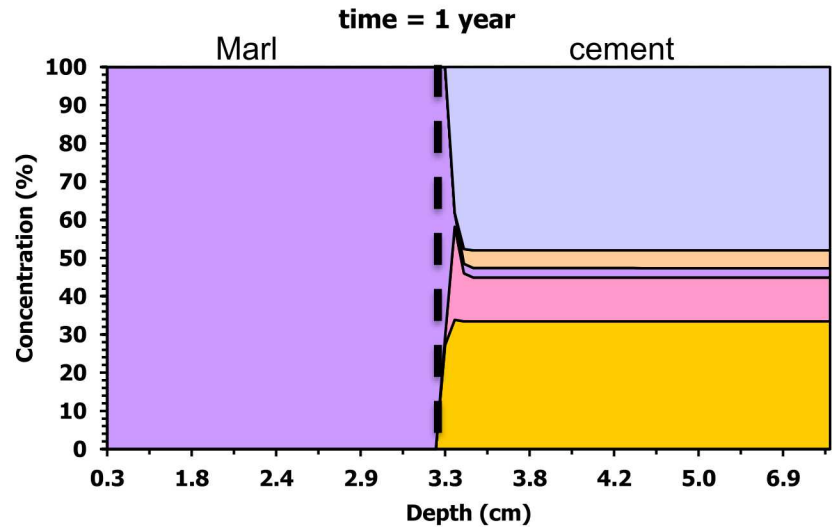
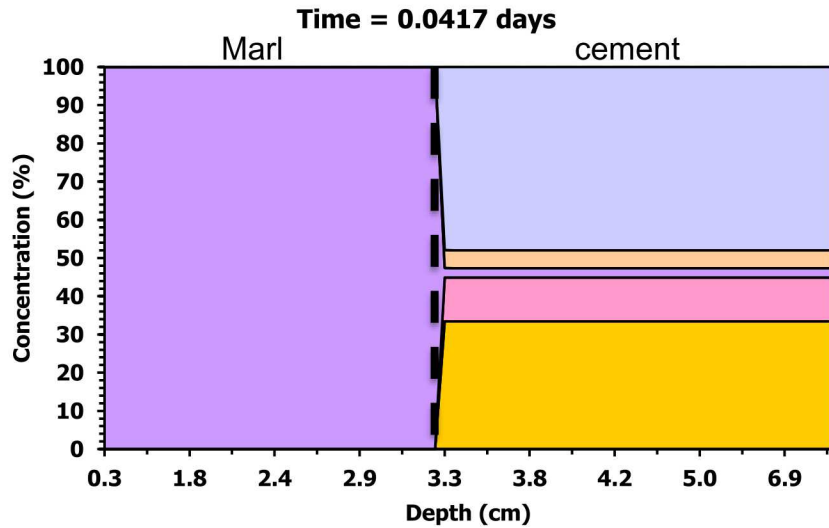
Cement – Marl Interface model

Interface model of Marl and OPC:



- Cement – OPC
- 9.1 cm monolith, 3.3 cm Marl
- 5 years, saturated conditions, 25 C
- Tortuosity – 87 and 30 for the Marl and OPC respectively (calibrated)
- Porosity – 31.7% and 8% for the Marl and OPC respectively
- No fluxes at boundaries – diffusion only (multi-ionic diffusion)
- Thermodynamic database – CEMDATA14 (Lothenbach et al. (2014))

Cement – Marl Interface model results - Ca

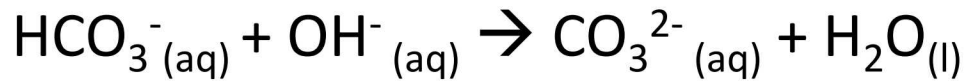


Carbonation front advanced 0.2 cm
in 5 years

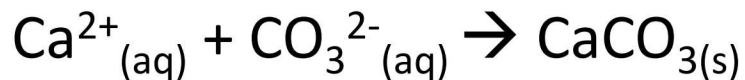
Cement – Marl carbonation

- Step 1 – diffusion of Bicarbonate from the marl to cement
- Step 2 – Bicarbonate reacts to form carbonate

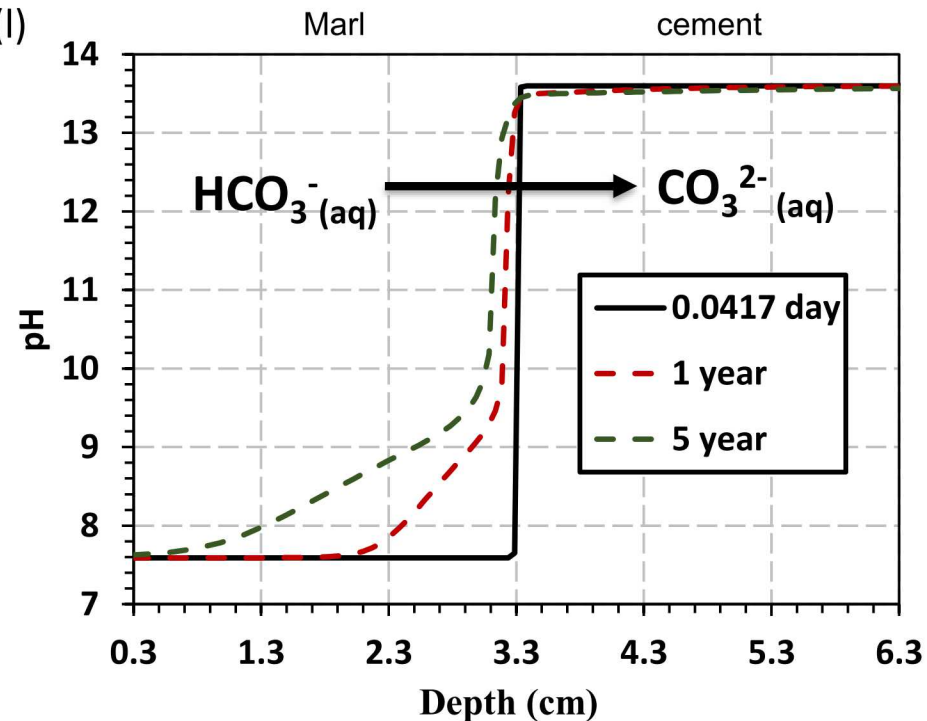
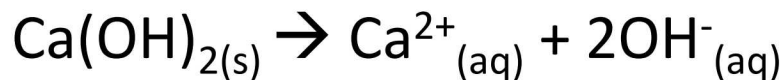
pore water	CO_3^{2-} (mol l ⁻¹)	Ca^{2+} (mol l ⁻¹)	pH
Marl	2.3	0.0005	7.7
Cement	0.0004	0.005	13.6



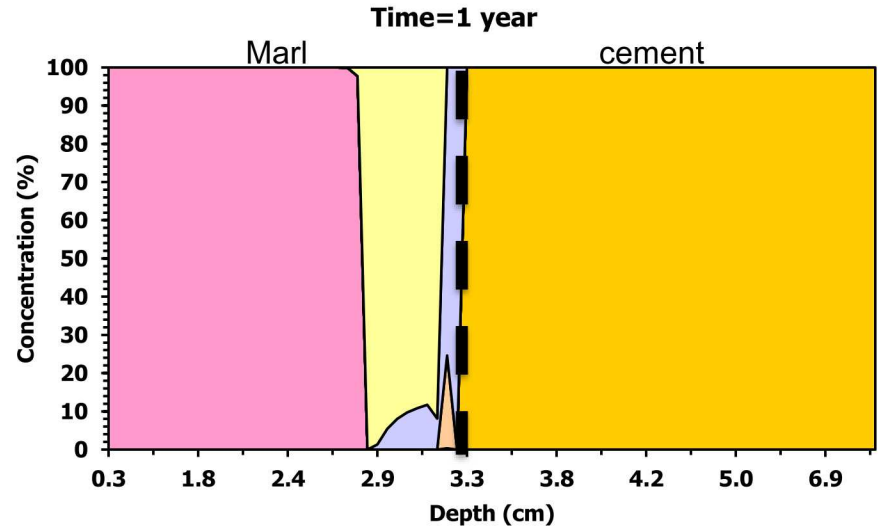
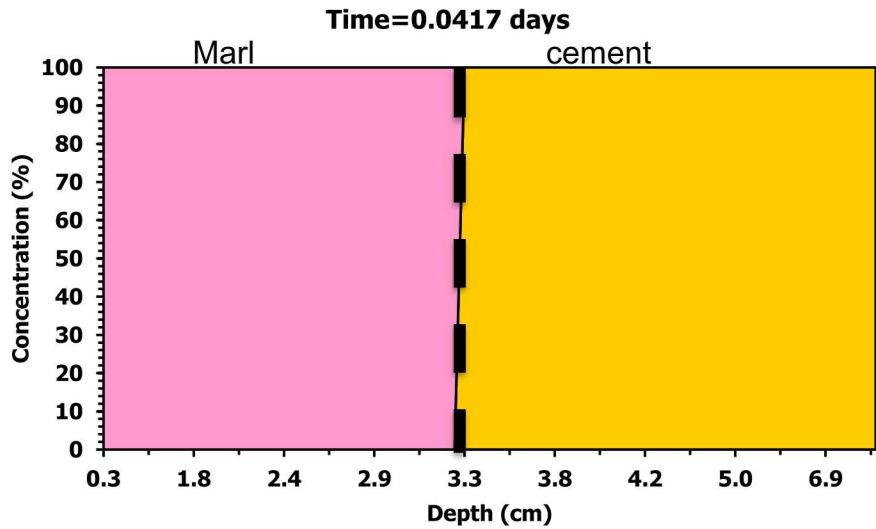
- Step 3 – pH decreases
- Step 4 – CaCO_3 precipitates



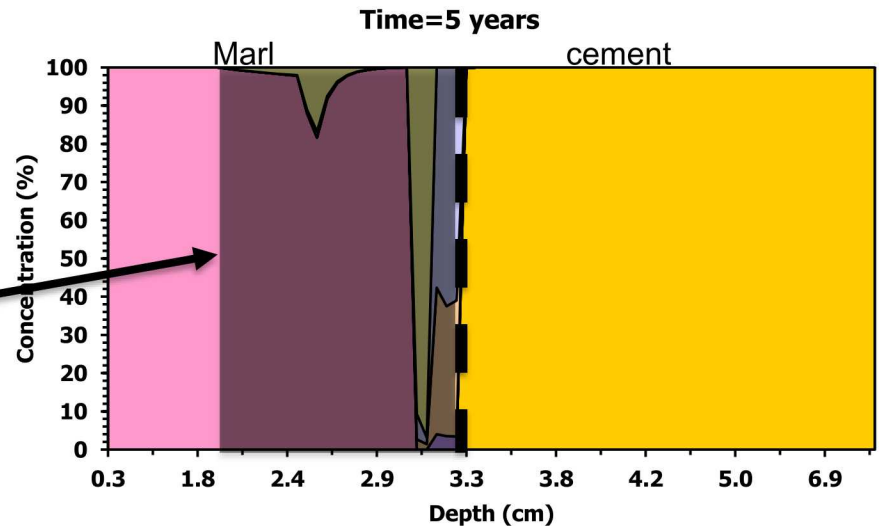
- Step 5 – Ca^{2+} and OH^- depletion
- Step 6 – portlandite dissolution.



Cement – Marl Interface model results - Si

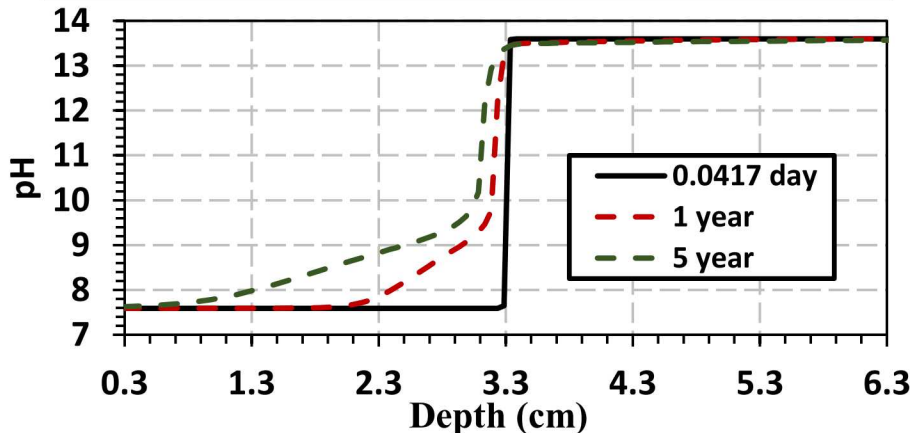
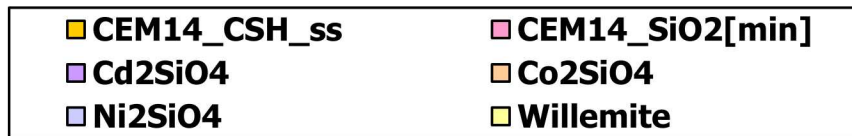
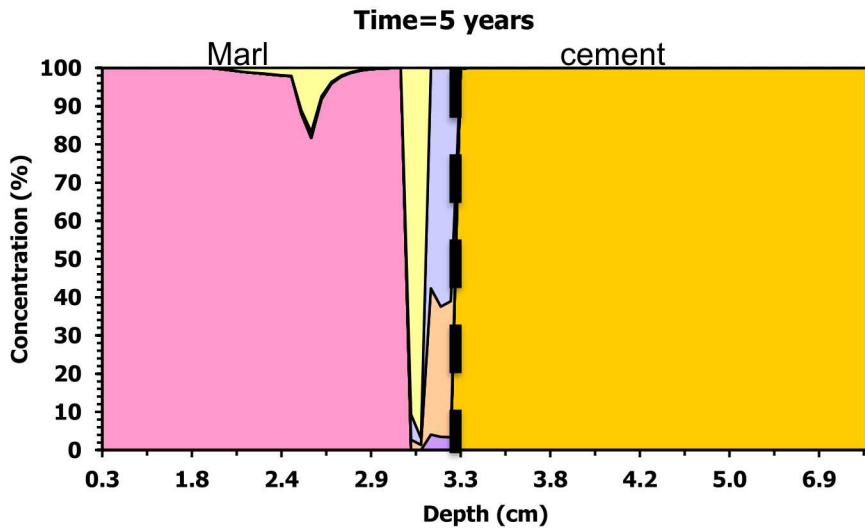


Alteration front advanced 1.3 cm in 5 years



Cement – Marl

Interface model results - Si



- Dissolved concentrations of Zn^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} and Si are higher (2-4 orders of magnitude) in the rock's pore water than in the OPC
- The precipitation of new silicate phases is a result of the diffusion of OH^- into the rock (pH increases)
- The distribution and precipitation of new silicate phases reflects differences in solubility products rather than differences in diffusion coefficients or concentration gradients

Willemite:

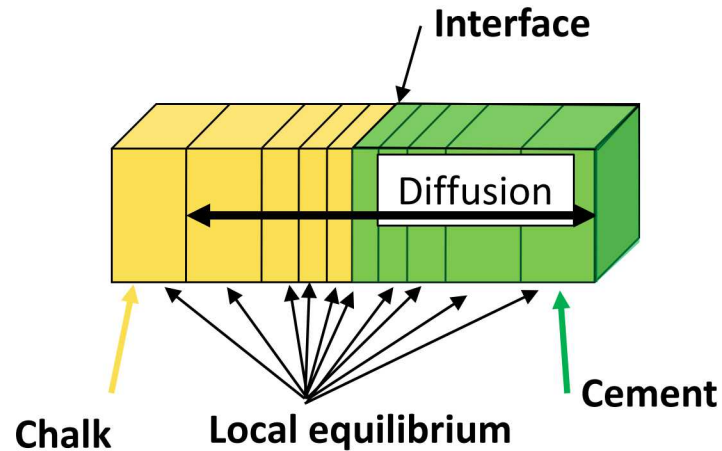
$$\Omega_{Zn_2SiO_4} = \frac{IAP}{K} = \frac{a_{Zn^{2+}}^2 \cdot a_{H_4SiO_4}}{a_{H^+}^4}$$

K (equilibrium constant)

	Zn_2SiO_4	Ni_2SiO_4	Co_2SiO_4	Cd_2SiO_4
K	$5 \cdot 10^{-16}$	$3 \cdot 10^{-15}$	$2 \cdot 10^6$	10^6

Cement – Chalk Interface model

Interface model of chalk and OPC:



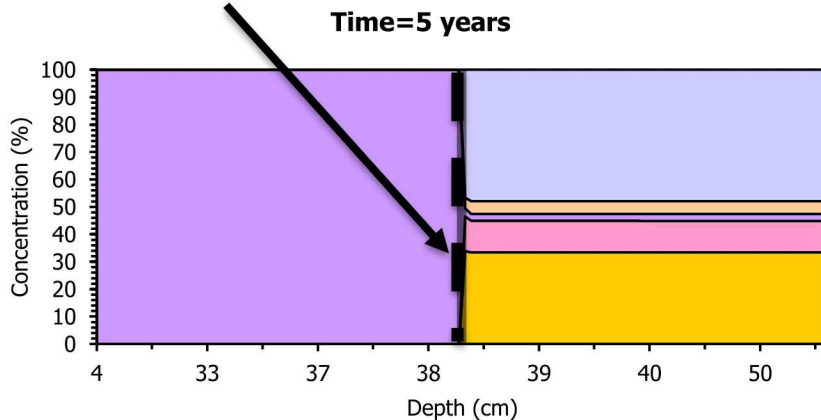
- Cement – OPC
- 76 cm monolith, 38 cm chalk
- 5 years, saturated conditions, 25 C
- Tortuosity – 50 and 30 for the chalk and OPC respectively (calibrated)
- Porosity – 6.8% and 8% for the chalk and OPC respectively
- No fluxes at boundaries – diffusion only (multi-ionic diffusion)
- Thermodynamic database – CEMDATA14 (Lothenbach et al. (2014))

Cement – Chalk Interface model results

Ca

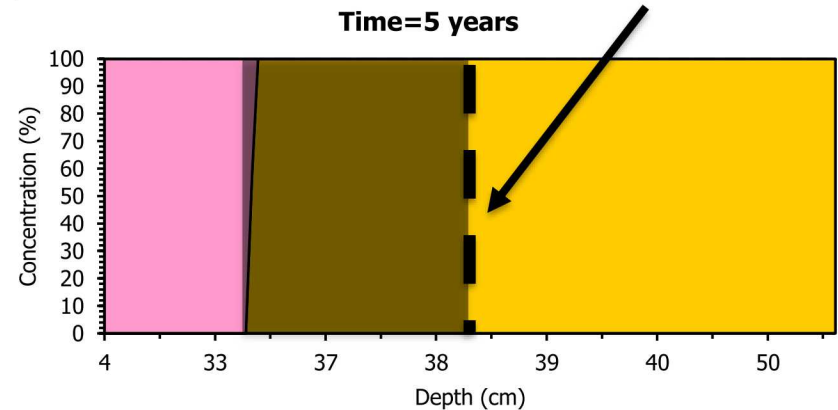
Si

Carbonation front advanced 0.05 cm in 5 years



- CEM14_CSH_ss
- ettr_ss
- CEM14_Calcite
- CEM14_monosulfoaluminate
- CEM14_portlandite

Alteration front advanced 2.6 cm in 5 years



- CEM14_CSH_ss
- CEM14_SiO2[min]
- Cd2SiO4
- Co2SiO4
- Ni2SiO4
- Willemite



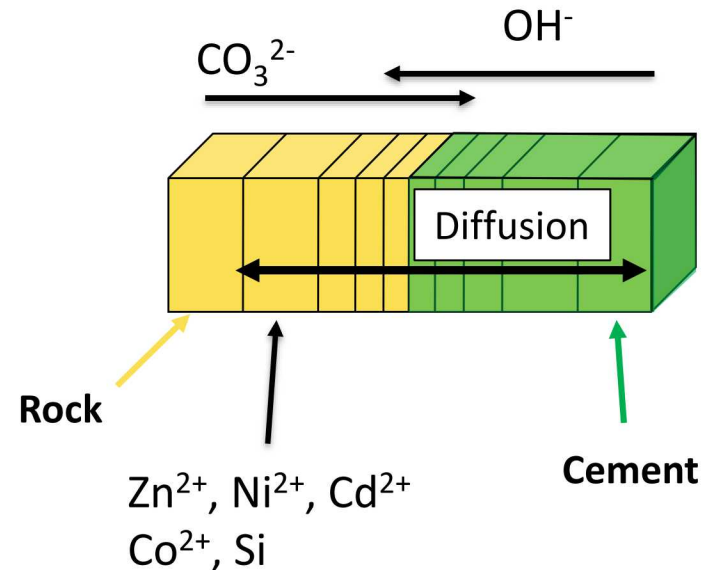
Conclusions



Cement – Chalk Vs. Cement – Marl:

- Thicknesses of altered and carbonated layers are different for two interfaces
- The thickness of altered rock is controlled by:
 1. constituents concentration in pore water
 2. solid phases equilibrium constants (K)
 3. pH
- The thickness of the carbonated layer is controlled by bicarbonate flux from the rock.
- Constituents flux is controlled by the ratio between porosity to tortuosity ($\frac{\phi}{\tau^2}$).
- $\frac{\phi}{\tau^2}$ is about 3 times higher for the marl than the chalk – it can be account for most of the difference.

	Carbonation front progress in 5 years (cm)	Alteration front progress in 5 years (cm)
Marl-OPC interface	0.2	1.2
Chalk-OPC interface	0.05	2.6





Acknowledgments

- SANL - Sandia National Laboratories
- CRESP - Consortium for Risk Evaluation with Stakeholder Participation

