Modeling Interfaces to Support Low-Level Waste Disposal System Performance Assessments

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Talk outline

- Motivation
  - Carbonation of concrete
  - Sulfate attack
- Objective
- Modeling methods
- Results
- Discussion
- Conclusions
- Future directions

Motivation

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- The U.S. Department of Energy (DOE) Savannah River Site (SRS) produced nuclear materials starting in the 1950s
- SRS has disposed of large volumes of low-level waste (LLW)
- The LLW is stabilized with grout and the solidified salt waste, denoted here as saltstone waste (SSW)
- SSW is disposed in large, concrete vaults referred to as Saltstone Disposal Units (SDUs)

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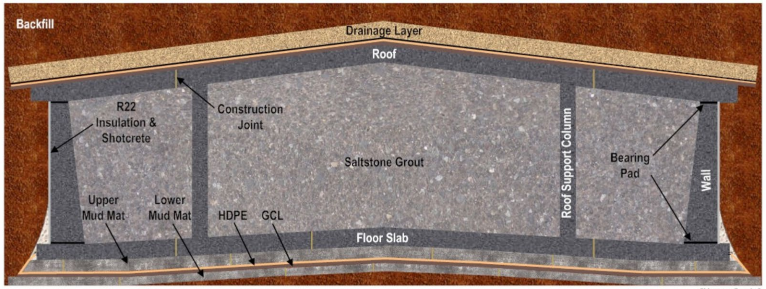
Motivation

- **Carbonation** and **sulfate attack** are important aging and possible degradation mechanisms that can lead to failure for LLW disposal structures

- Performance assessment (PA) is a required analysis of the long-term performance of closed SDUs
  - **Goal:** Reduce PA uncertainty and conservativeness by more accurately reflecting aging and degradation mechanisms that impact radionuclide release estimates



Carbonation of Concrete

- **Carbonation process:** Reaction of aqueous CO_2 with hydration minerals including portlandite, to form carbonated products and water
- Depletion of portlandite results in subsequent decalcification of C-S-H
- Leads to decrease in pH of the pore solution
- When pH < 9 → depassivation of embedded steel → corrosion and expansion → possible material cracking
- Mobility of radionuclides may increase in response to cracking and changes in pH, porosity, and mineralogical gradients

Transformation of gaseous CO_2 to carbonate

1) $CO_{2(g)} + H_2O_{(aq)} \rightarrow CO_3^{2-}{}_{(aq)} + 2H^+{}_{(aq)}$

Portlandite

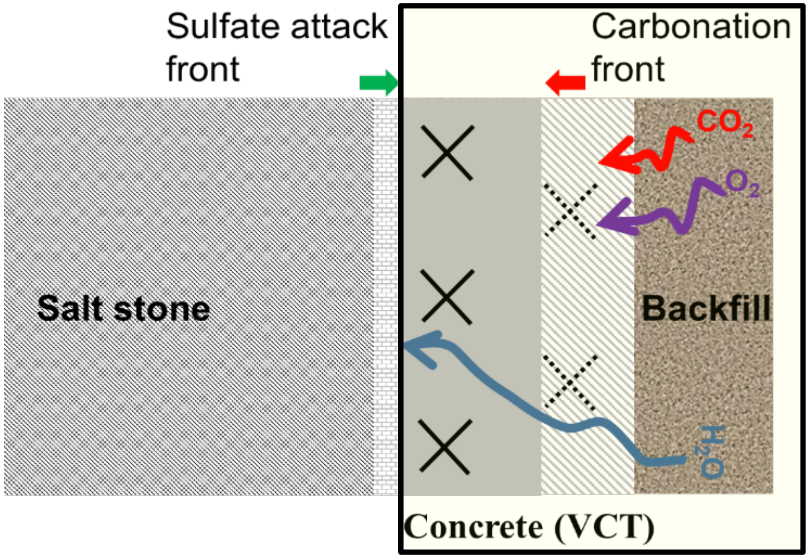
2) $Ca(OH)_{2(s)} + 2H^+{}_{(aq)} \rightarrow Ca^{2+}{}_{(aq)} + 2H_2O_{(aq)}$

Carbonated product

3) $Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CaCO_{3(s)}$

Decalcification of C-S-H

4) $x\text{CaO}\cdot\text{SiO}_2\cdot n\text{H}_2\text{O} + y\text{H}_2\text{O} \rightarrow (x-y)\text{CaO}\cdot\text{SiO}_2\cdot n\text{H}_2\text{O} + y\text{Ca(OH)}_2$



Sulfate Attack

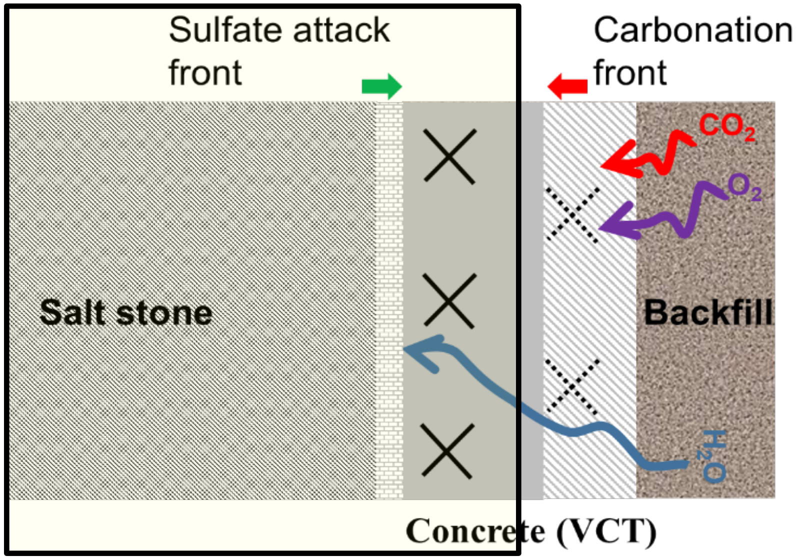
- **Sulfate attack** is usually attributed to the formation of sulfur-bearing phases (ettringite and/or gypsum) in concrete pore space as result of chemical reactions between hydrated cement products and solutions containing dissolved sulfate

- The predicted damage to the concrete is related to increases of volume occupied by the solid phases in the concrete and expansive pressure as a result of ettringite and gypsum formation

- In these LLW disposal vaults, sulfate is transported from the saltstone (liquid/solids) inside the vault to the saturated concrete pores

Reactants:
Portlandite V_m ~ 30 cm^3/mol
C-S-H solid solutions V_m = 30-80 cm^3/mol

Products:
Gypsum V_m = 75 cm^3/mol
Ettringite V_m ≥ 700 cm^3/mol



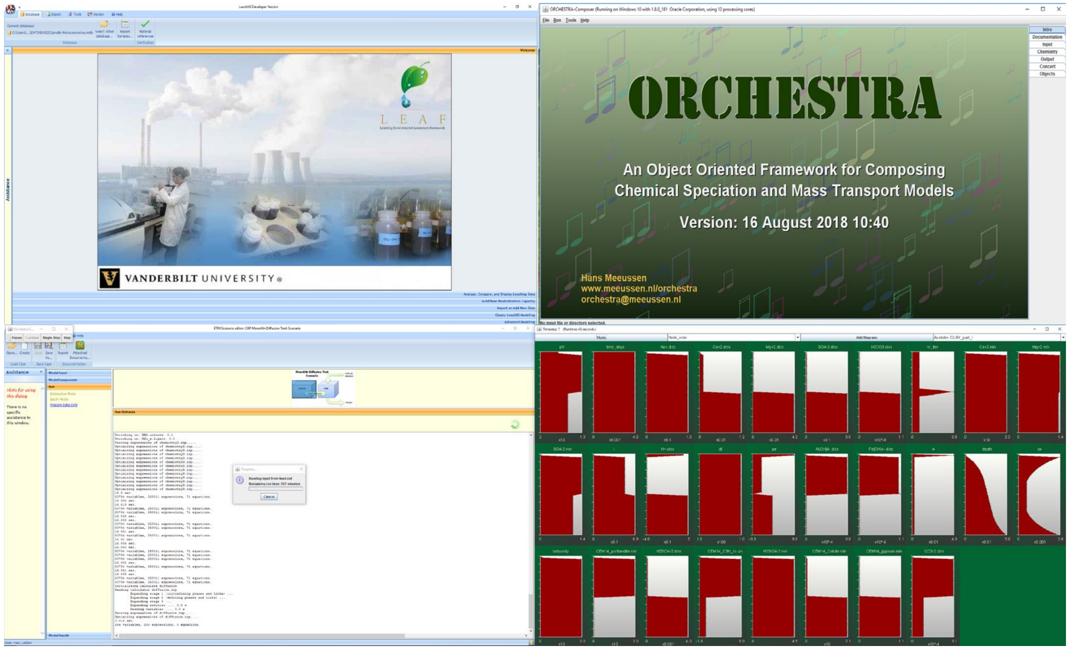
Objective

To simulate mass transport and reactions postulated to impact SDU vault performance:

- **Carbonation through vault exterior interface**
- **Sulfate attack through vault interior interface**

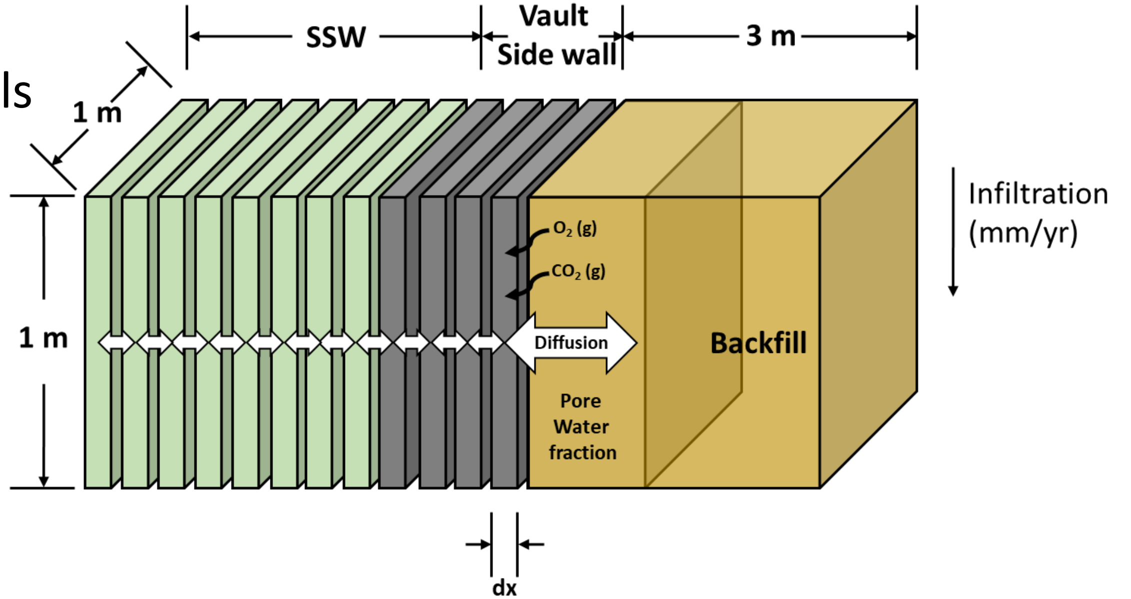
Methods – LeachXS/ORCHESTRA

- 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
- Mass transport, cement chemistry, geochemical speciation, liquid/solid partitioning, and multi-ionic diffusion



Conceptual Model

- **3 Materials:** SSW, VCT, and Backfill
- **2 interfaces:** SSW-VCT and VCT-Backfill
- Homogeneous, well-mixed cells
- **VCT (Vault Concrete)**
  - 15.24 cm
  - saturated
- **SSW (Saltstone)**
  - 1300 cm
  - saturated
- **Soil (Backfill)**
  - 300 cm
  - CO_2 $1.32 \cdot 10^{-5}$ mol/L (in equilibrium with atmospheric CO_2 387ppm)
  - 35% porosity
  - 50% saturation



- **Boundary conditions:**
  - SSW - no flux
  - Soil - refresh every 2.5 years, based on infiltration rates

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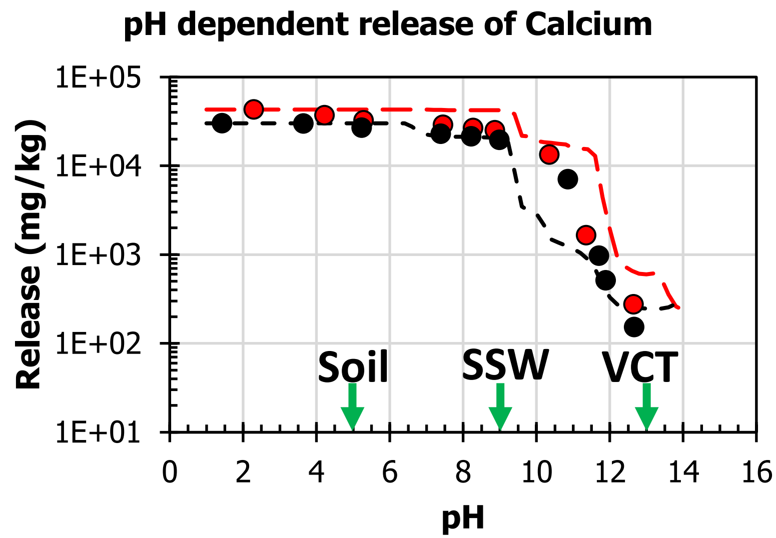
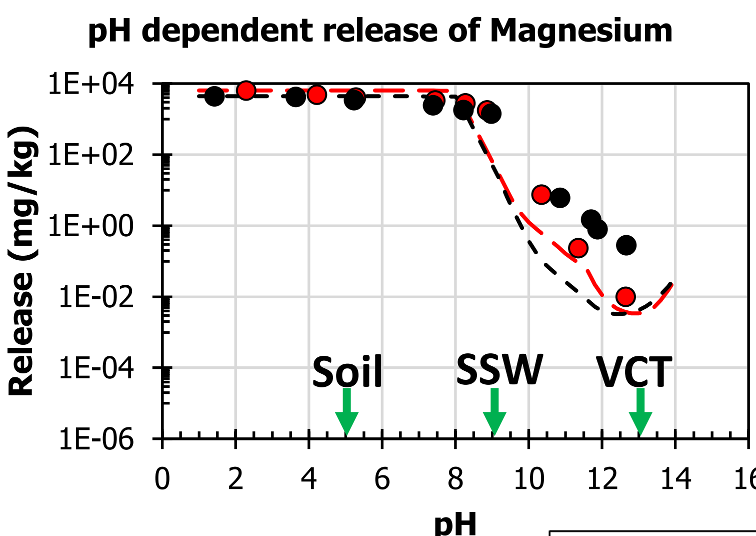
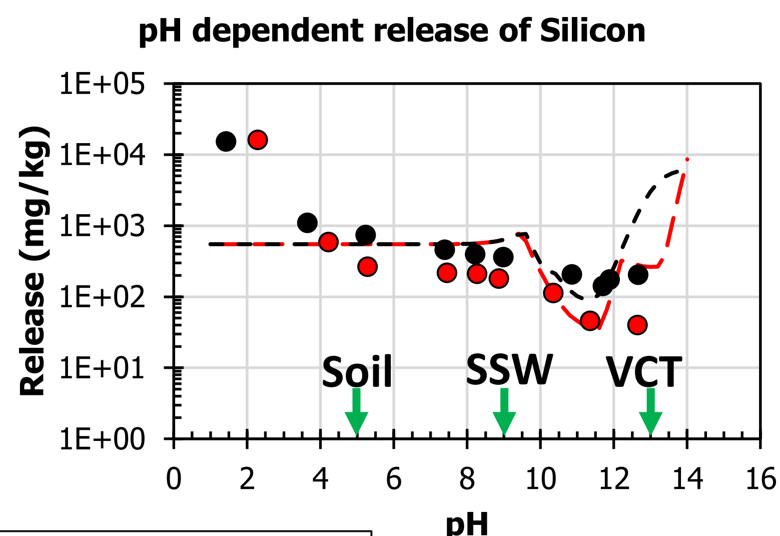
Methods - Mineral set

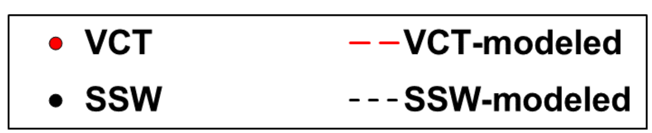
EPA Method 1313 –

- pH dependent leaching test
- liquid/solid partitioning (LSP) under equilibrium conditions
- pH ranging from <2 to 13
- liquid-to-solid ratio (L/S) of 10 mL/g-dry solid









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Methods - Mineral set

- **LeachXS/ORCHESTRA**
  - Solves system of equations:
    - Conversations of mass
    - Laws of mass action
  - Yields solid, aqueous and gaseous speciation
- **C-S-H**
  - Ideal solid solution with Tobermorite- and Jennite like end-members (Lothenbach et al., 2008)

$Mg(OH)_2$ Brucite	$Ca(OH)_2$ Portlandite	C3AH6 Hydrogarnet	C4Ac0.5H12 Hemicarbonate	C6As3H32 (Al-)Ettringite
$CaSO_4{\bullet}2H_2O$ Gypsum	$CaCO_3$ Calcite	C3FH6 Fe-hydrogarnet	C4Fc0.5H12 Fe-hemicarbonate	C6Fs3H32 Fe-ettringite
SiO_2 (am) Amorphous Silica	C2ASH8 Strätlingite	C3AS0.8H4.4 Siliceous Hydrogarnet	C4AcH11 Monocarbonate	C6Ac3H32 Tricarboalumin ate
$Al(OH)_3$ (am) Amorphous Gibbsite	C2FSH8 Fe-strätlingite	C4AH13 Hydroxy AFm	C4FcH12 Fe-monocarbonate	M4AH10 Hydrotalcite
Al_2O_3 Alumina	C2AH8 Unnamed metastable phase	C4FH13 Fe-hydroxy AFm	C4AsH12 Monosulfate	M4FH10 Fe-hydrotalcite
$Fe(OH)_3$ (mcr) Microcrystalline Fe(OH)3	C2FH8 Unnamed metastable phase	Solid Solution: C1.67SH2.1 Jennite	C4FsH12 Fe-monosulfate	M4AcH9 CO3-hydrotalcite
	$CaSO_4$ Anhydrite	C0.83SH1.3 Tobermorite		

* **Notation:** C=CaO, A=Al_2O_3, F=Fe_2O_3, S=SiO_2, H=H_2O

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Physical parameters

	Porosity (∅)	Tortuosity factor (τ)
VCT	13.2%	189
SSW	65%	70
Soil	35%	*

* The soils in SRS are predominately sandy and possess a high infiltration rate and low runoff potential

$$D_{eff} \propto \frac{\emptyset}{\tau^2}$$

D_{eff} is the effective diffusivity (m^2 sec^{-1})

∅ is the porosity (fraction)

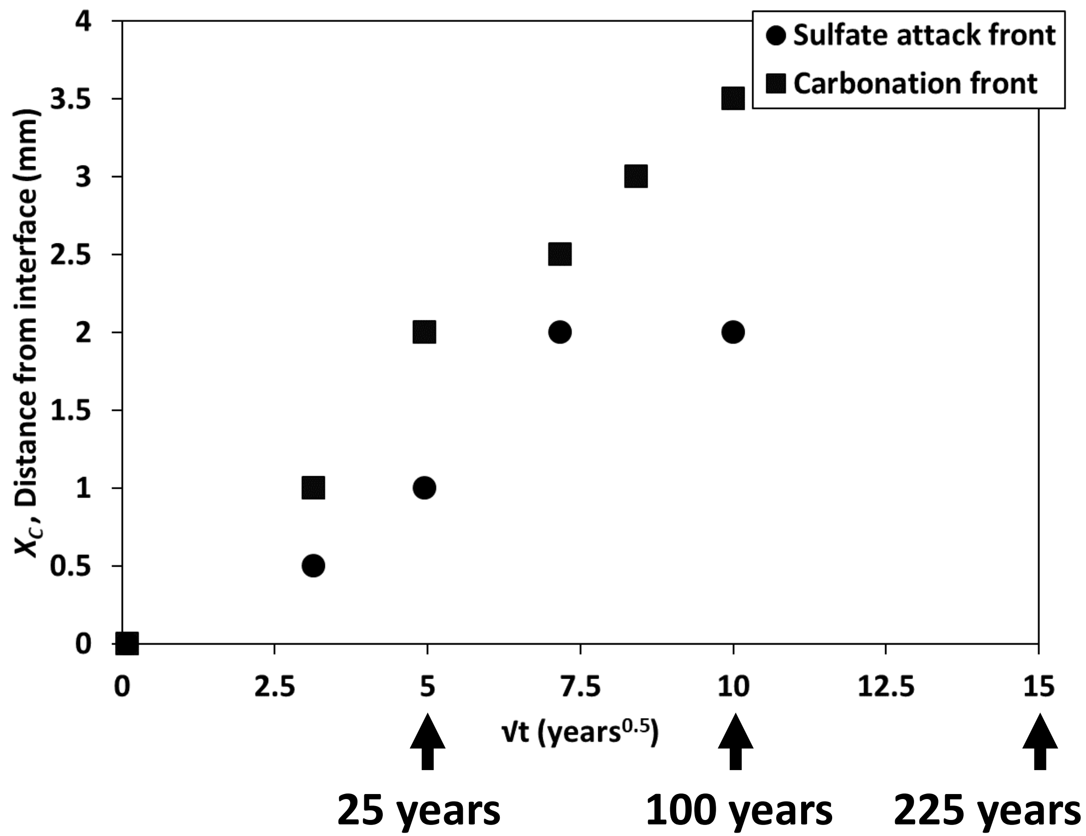
τ is tortuosity (m m^{-1})

Data from:

- SIMCO Technologies Inc. Washington Savannah River Company Subcontract AC81850N Report - Vault Concrete Characterization. SIMCO Technologies Inc. Quebec Canada, March 2012.
- SIMCO Technologies Inc. Washington Savannah River Company Subcontract AC48992N Report - Characterization of a Wasteform Mixture. SIMCO Technologies Inc. Quebec Canada, June 2010.

Results

- **After 100 years:**
  - Carbonation front is about 3.5 mm from the interface with the backfill material
  - Sulfate attack front located about 2 mm from the interface with SSW
- Sulfate attack front propagated slower than that of the carbonation front
- The location of carbonation and sulfate attack fronts show close to linear dependency during first 100 years of simulated time

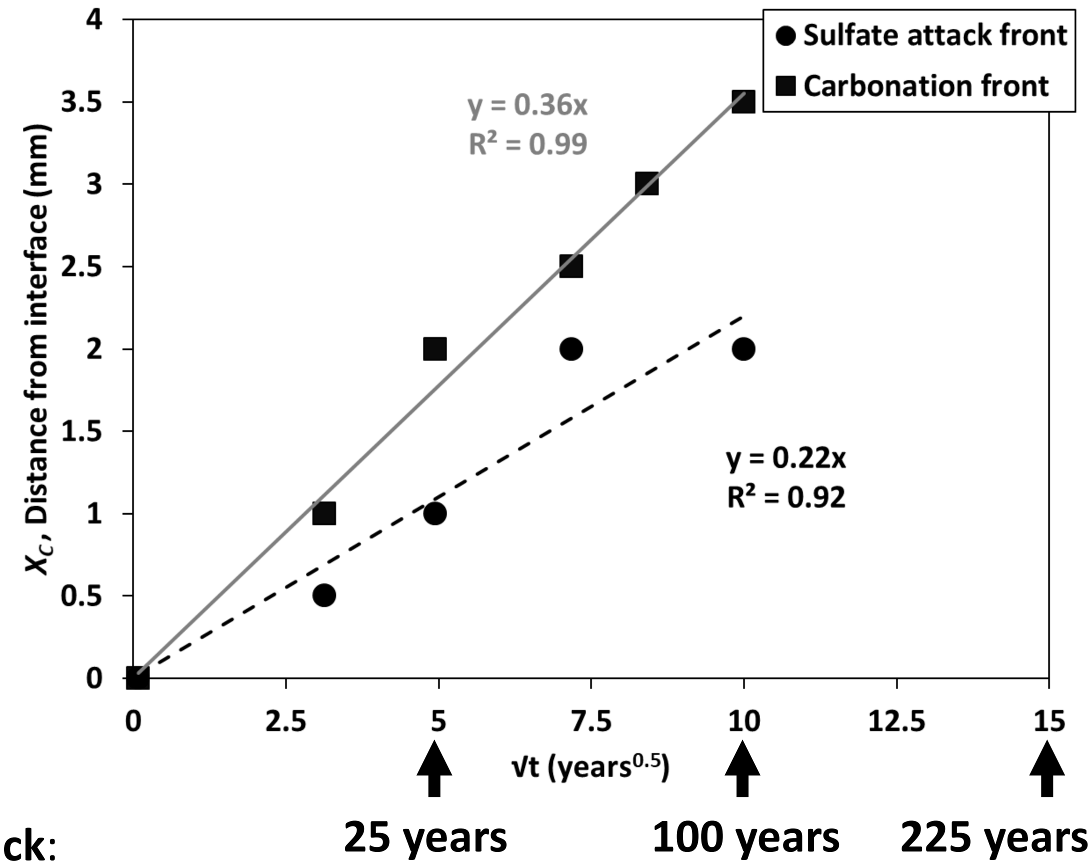


Results

- The propagation of the concrete carbonation front as a function of time can be described using a mechanistic model of Papadakis and Fardis (1989)
- Model that considers mass transport, cement chemistry, and reaction kinetics

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

X_c – front's location
A - proportionality constant
t - time



Carbonation:
$X_c = 0.36\sqrt{t}$

A_c = 0.36 mm/yr$^{0.5}$

Sulfate attack:
$X_S = 0.22\sqrt{t}$

A_S = 0.22 mm/yr$^{0.5}$

CRESP Estimation the time of concrete failure

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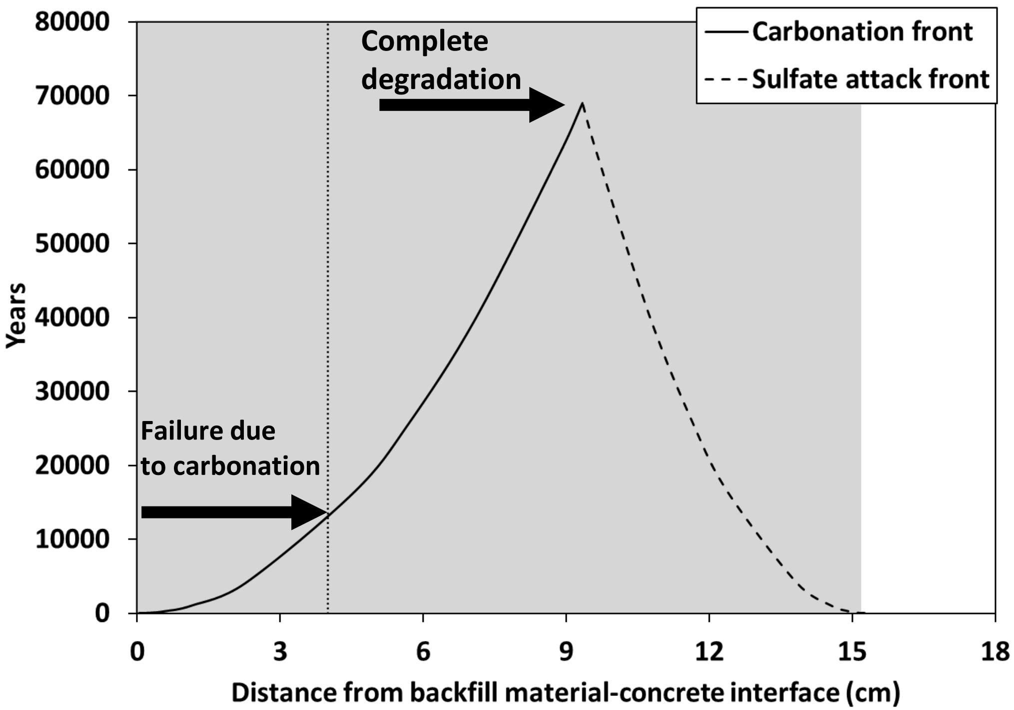
- Complete degradation of vault concrete is *assumed* when carbonation and sulfate attack fronts meet
- Concrete failure is *assumed* when the carbonation front or sulfate attack front fully penetrates through to the rebar in concrete (concrete cover thickness)
- The minimum depth of concrete cover to rebar in VCT is assumed to be 40 mm
- Estimated time of failure:
  - Complete degradation: 69,000 years
  - Carbonation: 12,300 years
  - Sulfate attack: 33,000 years



Discussion

- Flach and Smith (2013) estimated degradation time scale as a result of carbonation across backfill material-VCT interface near saturated conditions for SRS SDUs
- Using analytical solutions combined with numerical simulations.
- They calculated a range of values for A_C and A_S based on SDU vaults and location

	A_C mm/yr$^{0.5}$	A_S mm/yr$^{0.5}$
Flach and Smith	0.27	0.11
Present study	0.36	0.22

Conclusions

- Carbonation and sulfate attack fronts advance rates were estimated based on reactive-transport model
- The advancement rates of reaction fronts are proportional to square root of time Over the first 100 years of simulated time
- The time of concrete failure was evaluated in three different degradation scenarios:
  1. Carbonation and sulfate attack fronts intersect - 69,000 years
  2. Carbonation front advances through the 40 mm of concrete cover – 12,300 years
  3. Sulfate attack front advances through 40 mm of concrete cover – 33,000 years
- The shortest duration to concrete degradation (significant impact) was predicted when the carbonation front advanced through the 40 mm of concrete cover
- These predictions are generally an order of magnitude longer than predictions done before but they agree with A_C and A_S Flach and Smith showed

Future directions

Future studies will consider the effects of:

1. Replacing the CEMDATA07 (Lothenbach et al., 2008) thermodynamic database with the more recent CEMDATA18 (Lothenbach et al., 2019) database on the predicted results
2. Transport phenomena such as water and associated ionic transport due to different capillary pressures across the concrete-backfill material interface
3. Sensitivity analysis:
   - Exterior carbon dioxide/carbonate concentrations
   - pH and sulfate content in saltstone

Acknowledgments

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