Monitoring of Geological CO_2 Sequestration Using Isotopes & PFTs

Project Number FEAA-045 (Task 1)

Joachim Moortgat[2]

DR Cole[2], DE Graham[1], SM Pfiffner[3], TJ Phelps[3]

1 Oak Ridge National Laboratory

2 The Ohio State University

3 The University of Tennessee Knoxville

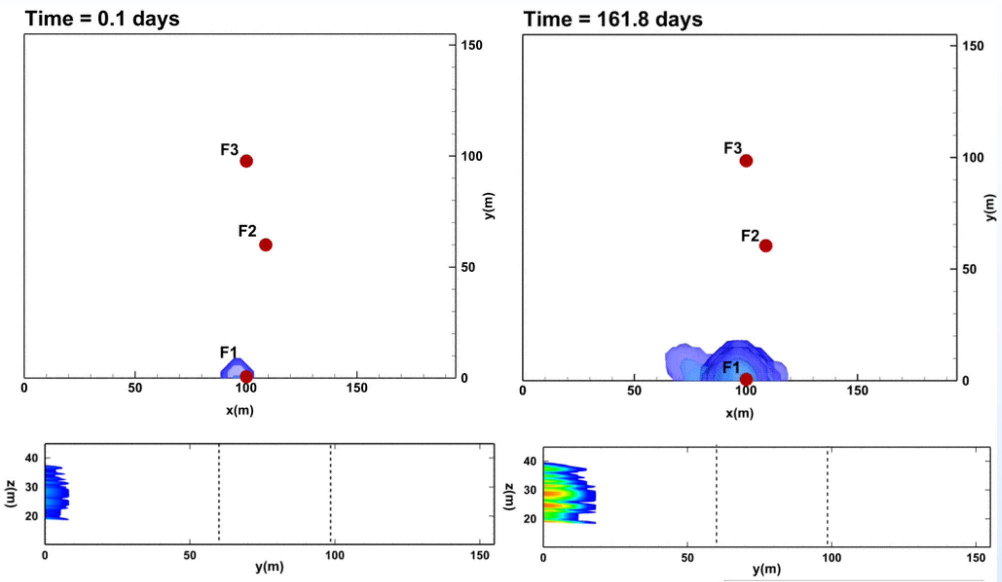
U.S. Department of Energy

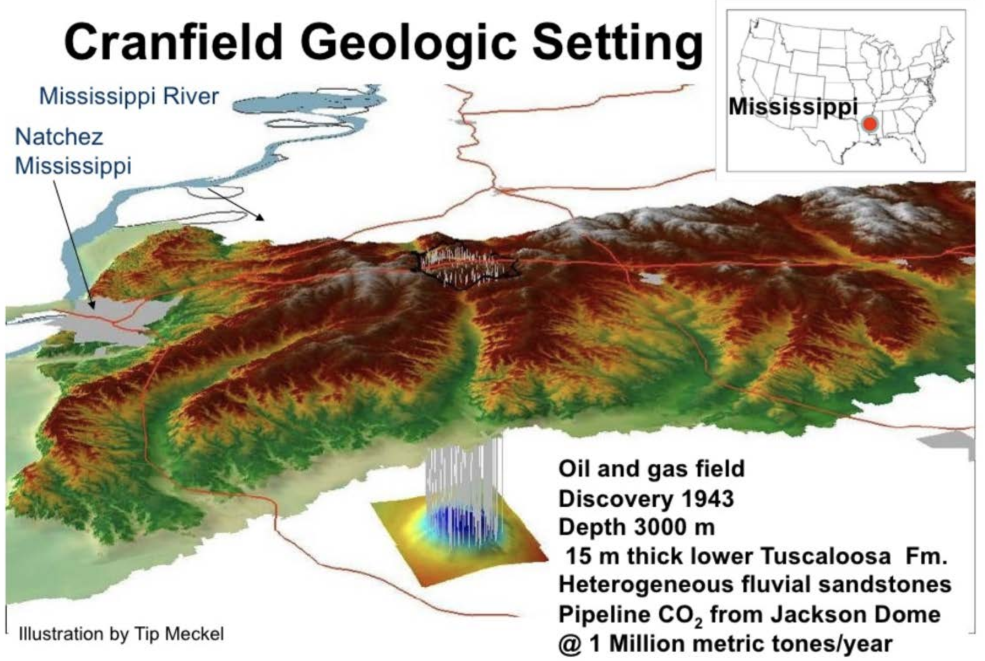
National Energy Technology Laboratory

Addressing the Nation's Energy Needs Through Technology Innovation – 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting

August 26-30, 2019

Presentation Outline

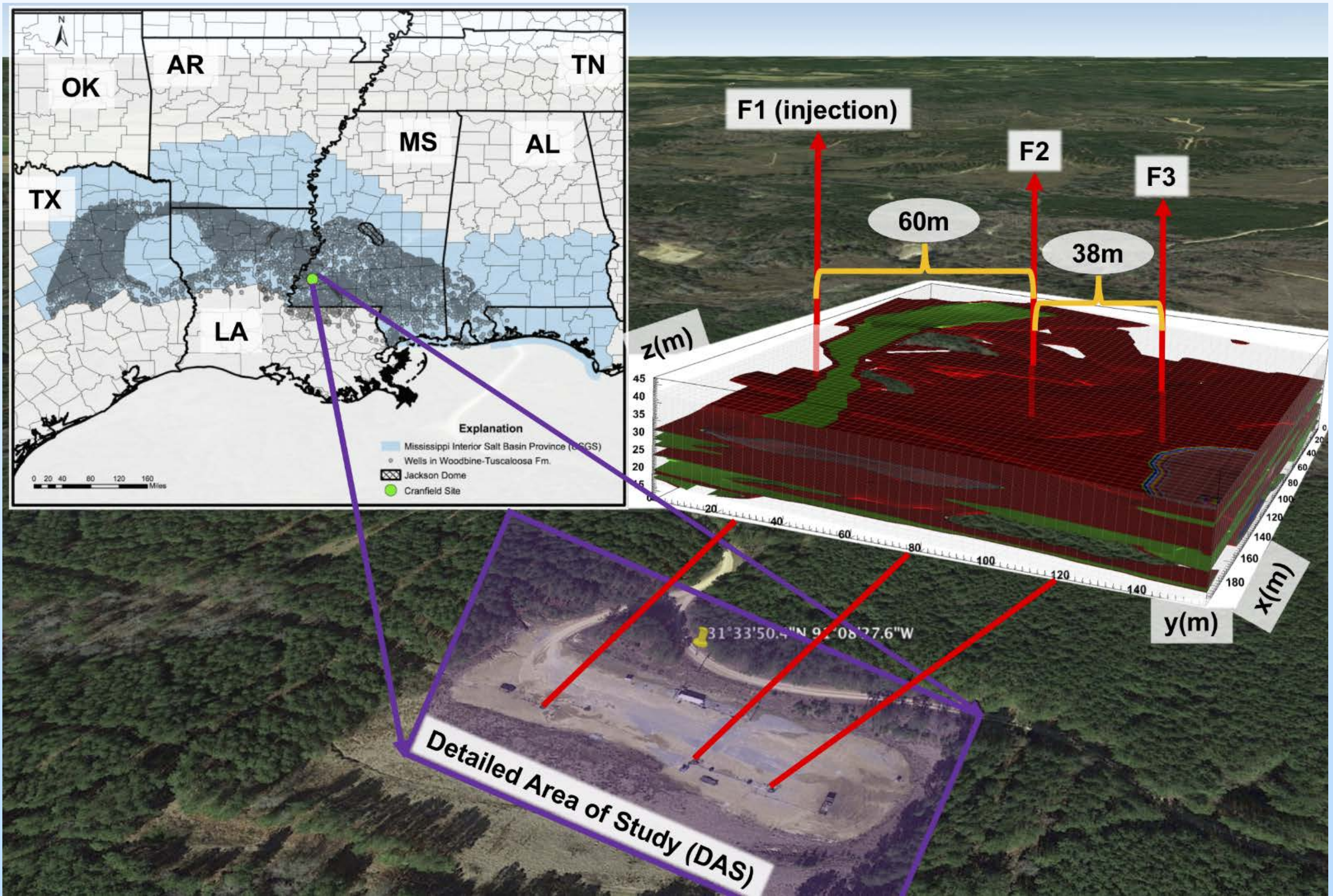




- Overview of project
- Past accomplishments (Task 1)
- Current technical status (Task 1)
- Lessons learned
- Synergistic opportunities
- Project summary

Overview of Project

- **Task 2** (Thur. 4.30pm, Graham ORNL): Investigate perfluorocarbon tracers (PFT), isotopes, other novel geochemical signals to interrogate subsurface (at Cranfield).

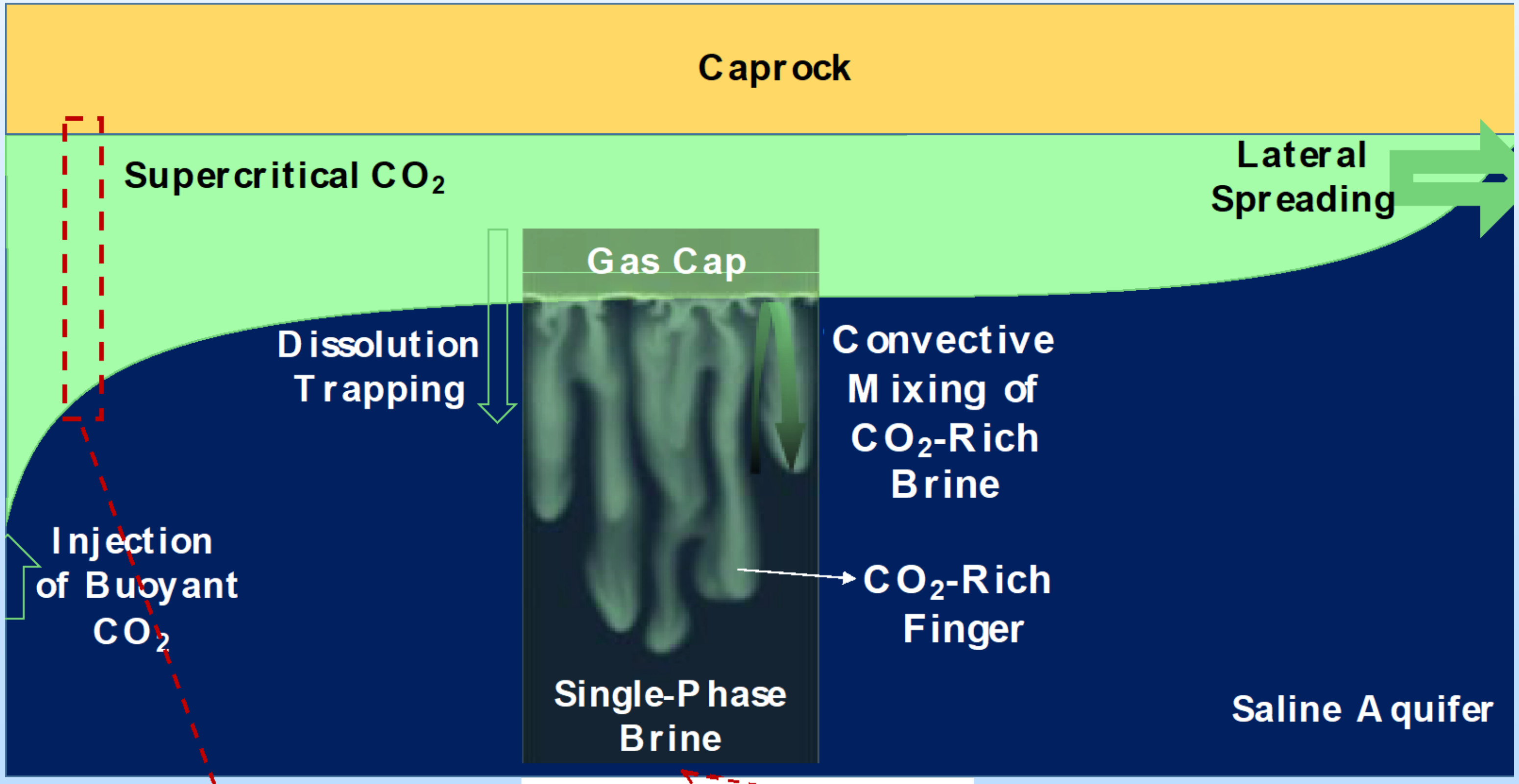


- **Task 1**: Incorporate data into numerical models to
  - Better interpret field data, e.g., 3D CO_2 plume development,
  - Predict long-term evolution of fluids and formation,
  - Apply lessons learned from prior pilot tests to other/future projects.

Objective

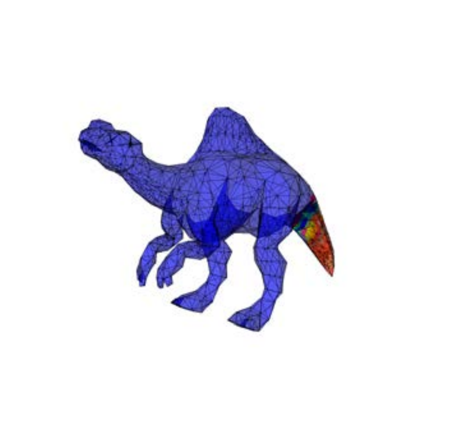
- Constrain **structural, solubility, and chemical** trapping mechanisms that guarantee storage permanence, through novel subsurface signals & modeling.
  - Non-trivial migration patterns in heterogeneous formations
  - Diffusion driven convection and cross-flow into low-perm. facies
  - Chemically driven mineralization of CO_2 and formation alterations

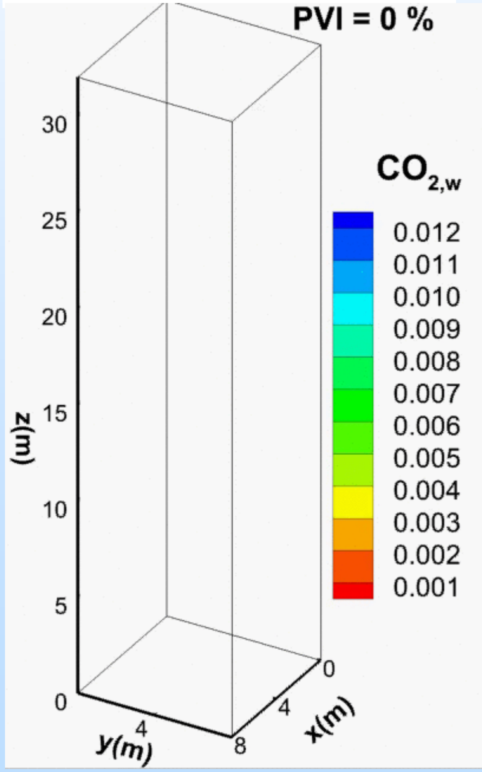
- Iteratively coupled workflow of field data and modeling



Modeling Tools

- Unique combination of capabilities in **Osures**:
  - Higher-order FE methods for flow and transport: allow unstructured grids, tensor permeability, discrete fractures, strong heterogeneity
  - Low numerical dispersion (e.g., resolves small-scale onset of instabilities)
  - Cubic-plus-association (CPA) equation of state (non-ideal) phase behavior modeling of water, CO_2, hydrocarbons, tracers (capture, e.g., competitive dissolution and brine compressibility)
  - Fickian diffusion with self-consistent composition + T + p -dependent full matrix of diffusion coefficients for multicomponent multiphase fluids
  - Capillary-driven flow with composition + p -dependent surface tension
  - ***New*** Reactive transport by coupling to iPHREEQC geochemistry

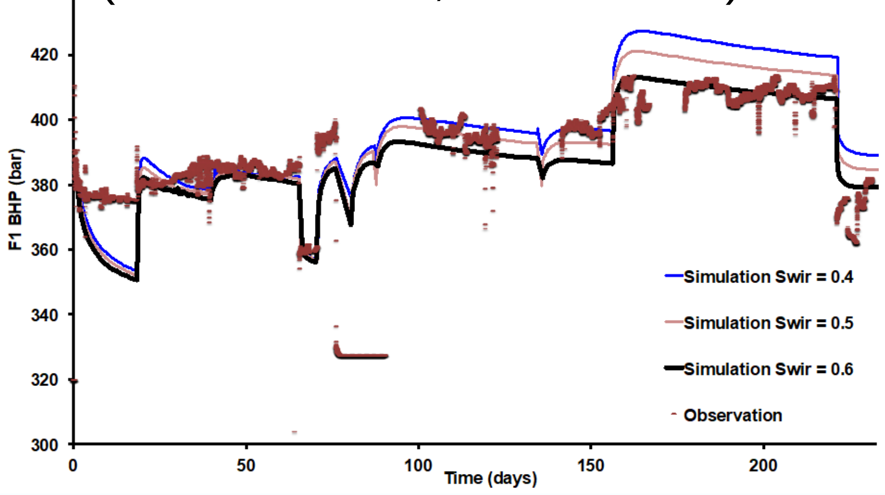




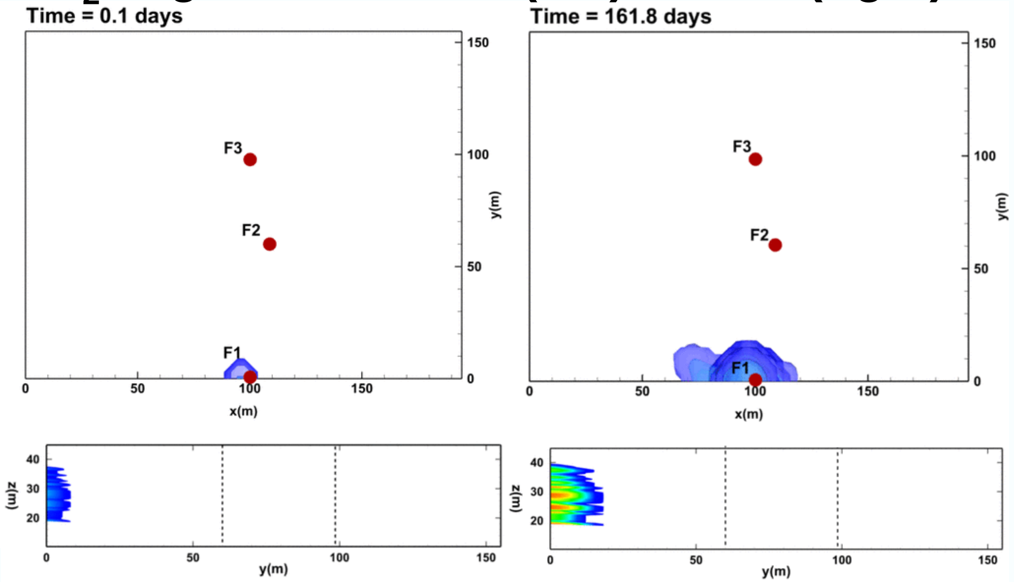
Prior Accomplishments

Pressure response in injection well

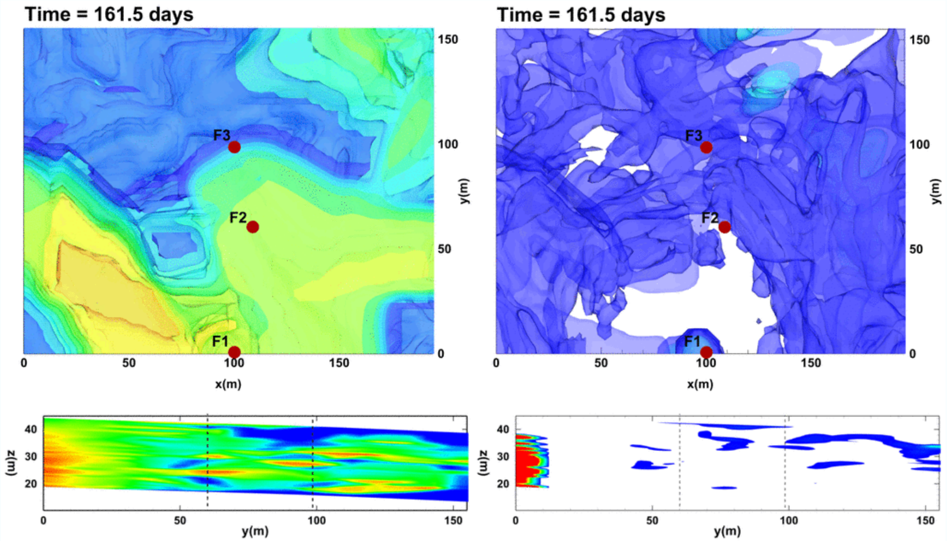
(Soltanian et al., *IJGGC* 2016)

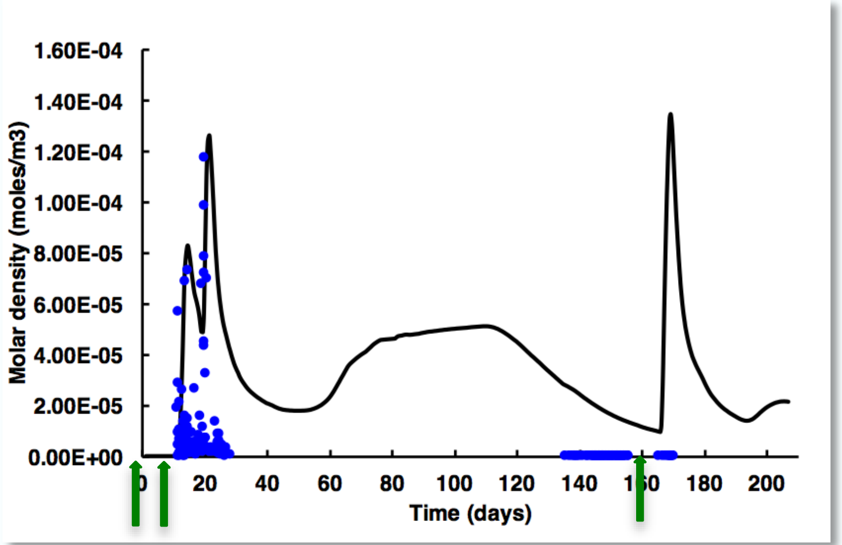


CO_2 migration in 2009 (left) & 2010 (right)



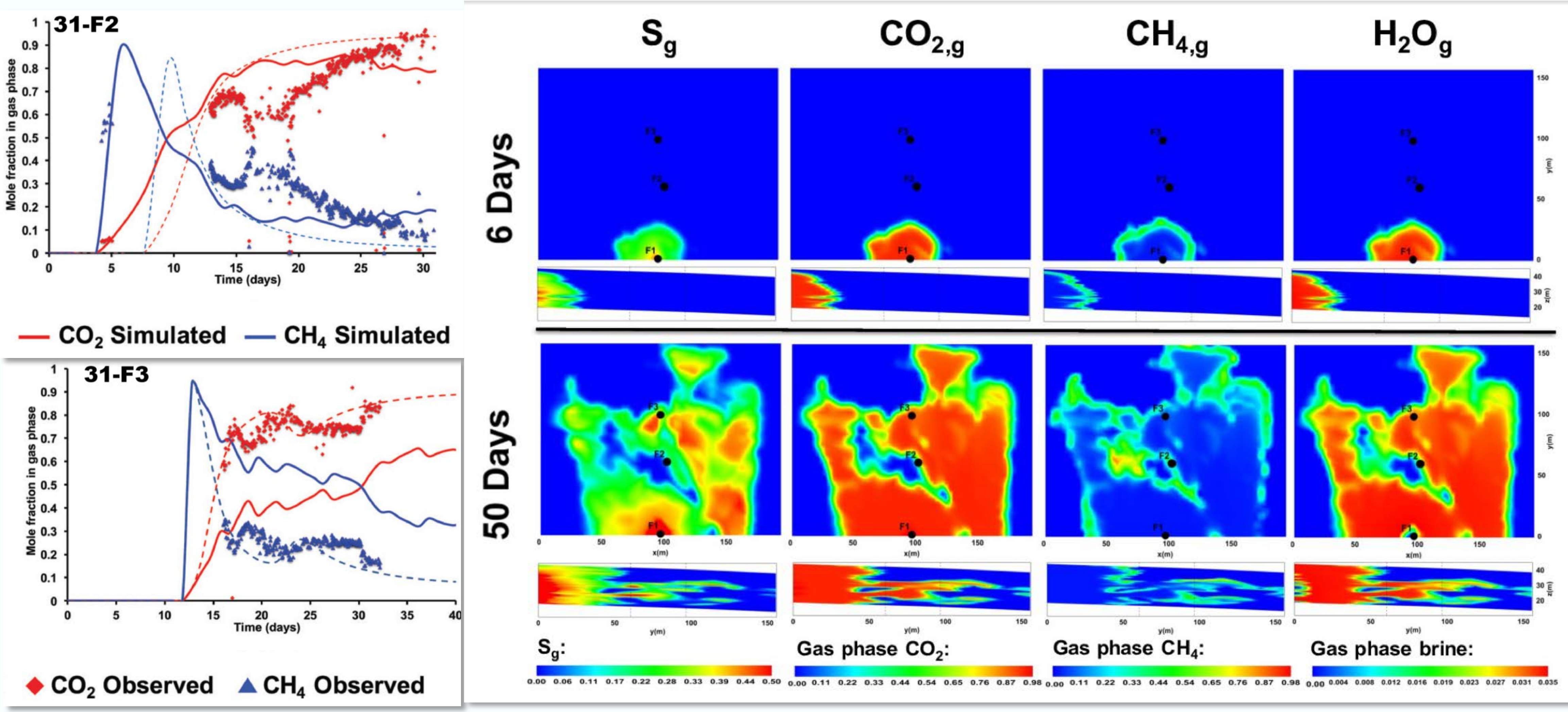
CO_2 and PFC tracer migration (Soltanian et al., *GGST* 2018)





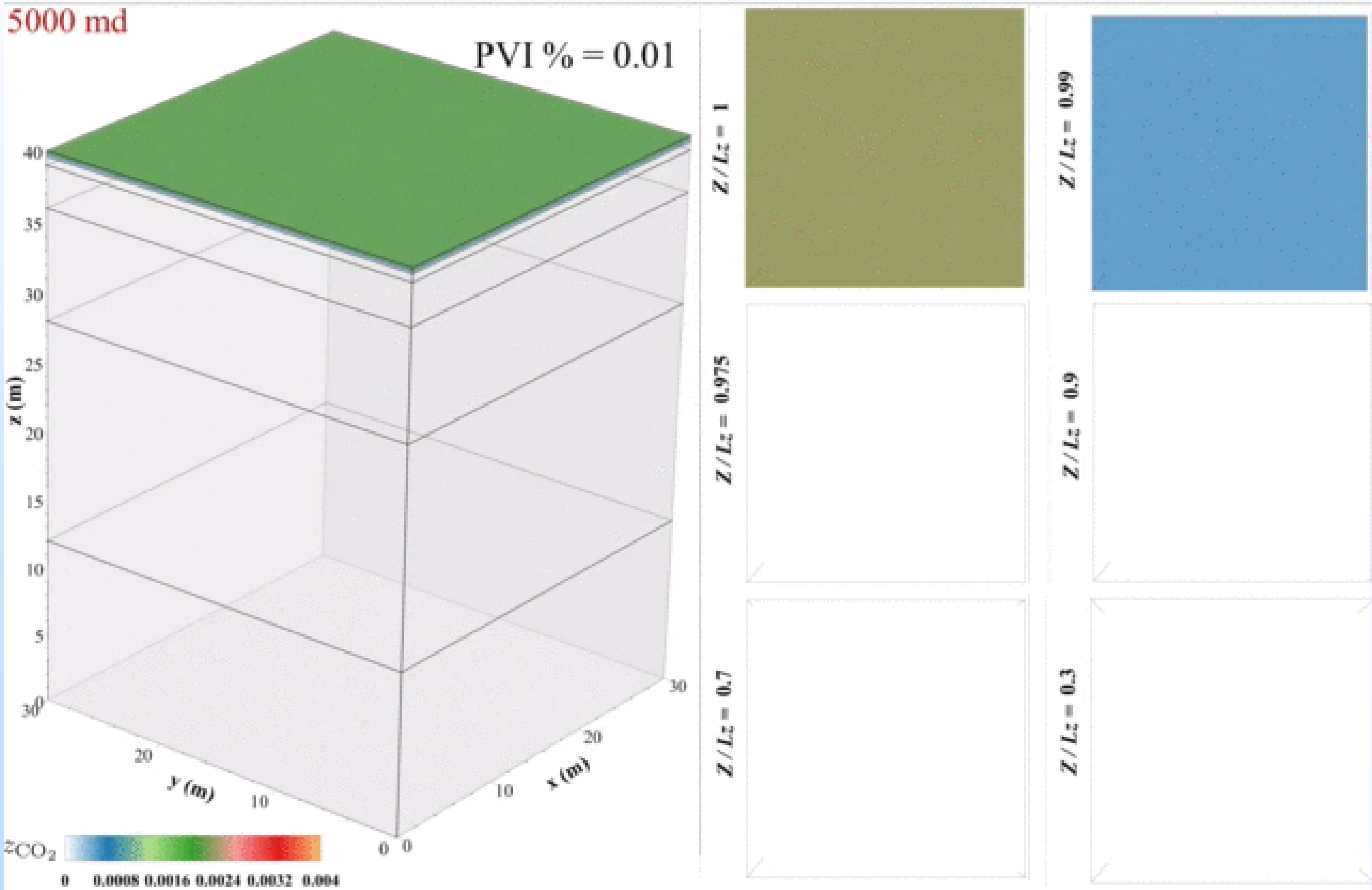
Prior Accomplishments

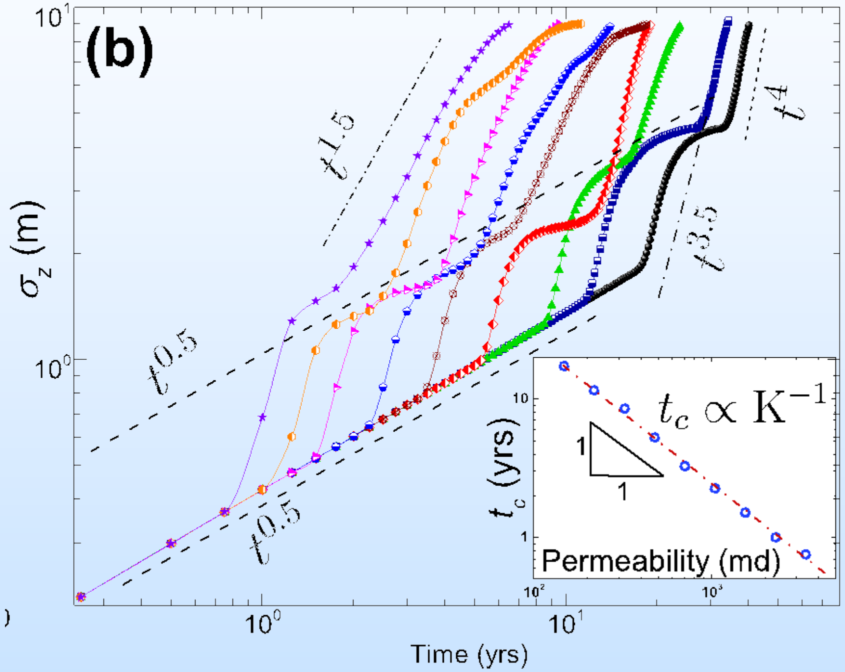
Exsolution and migration of pre-existing dissolved methane (Soltanian et al., *Groundwater* 2018)



Prior Accomplishments

Universal scaling behavior of gravito-convective mixing of dissolved CO_2





1. Soltanian et al., *Sci Rep.* 2016
2. Amooie et al., *GRL* 2017
3. Soltanian et al., *ES&T* 2017
4. Amooie et al., *GGGG* 2017
5. Dai et al., *Applied Energy* 2018
6. Amooie et al., *Phys Rev E*, 2018

Technical Status

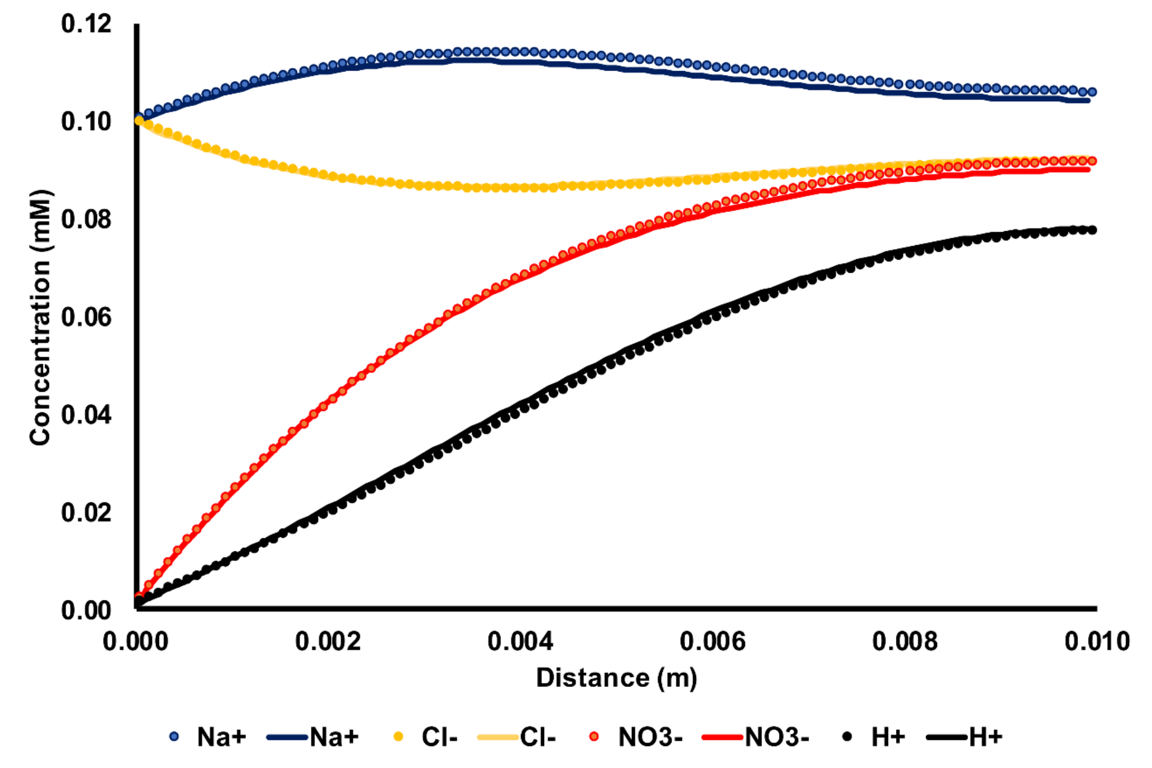
- 2019: Coupled **Osures**, higher-order FE simulator for 3D multiphase multicomponent compositional (EOS-based) convection, diffusion, capillarity, gravity, dispersion, fractures to **iPHREEQC** for geochemistry.

- PHREEQC is open source, well validated, offers interface to other flow simulators (only 1D transport itself).

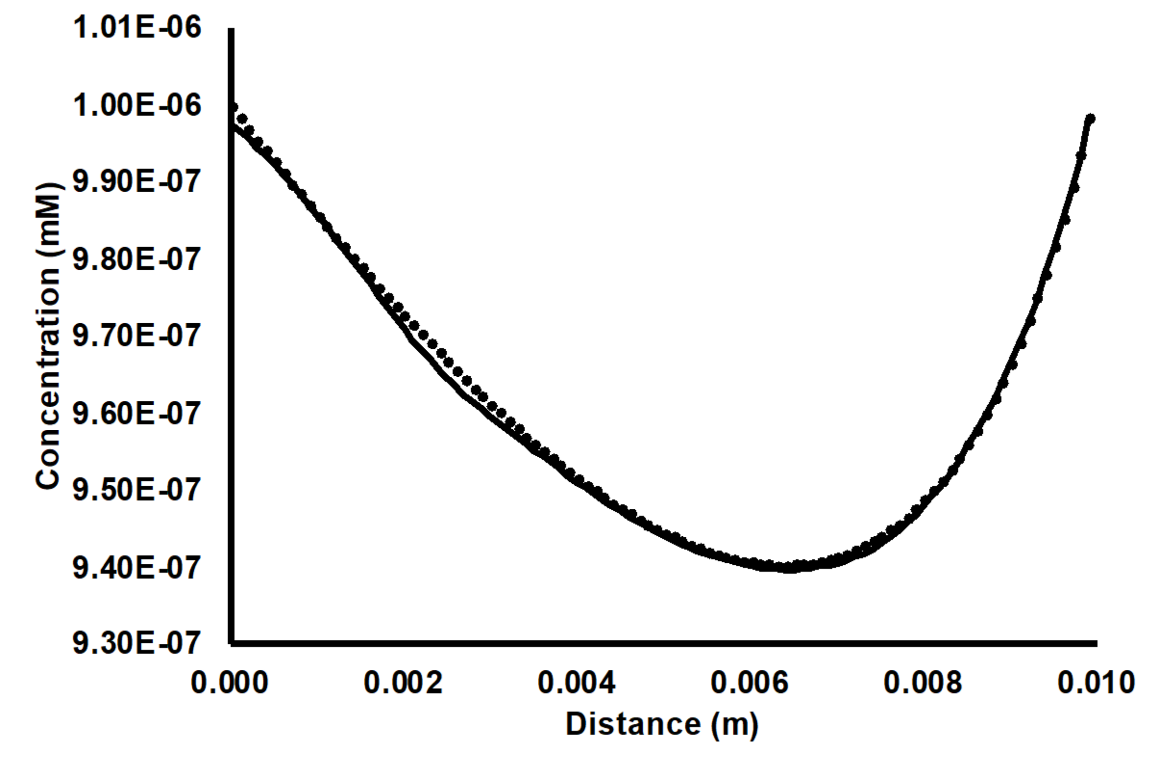
- Currently, full Osures capabilities, but 1-phase chemistry. Multiphase in FY2020.

Benchmarking

1. Electrochemical migration (Nernst-Planck diffusion[1]) of Na^+, Cl^-, H^+, NO_3^-.
   Modeled with CrunchFlow, MIN3P, PHREEQC (symbols), **Osures** (solid).



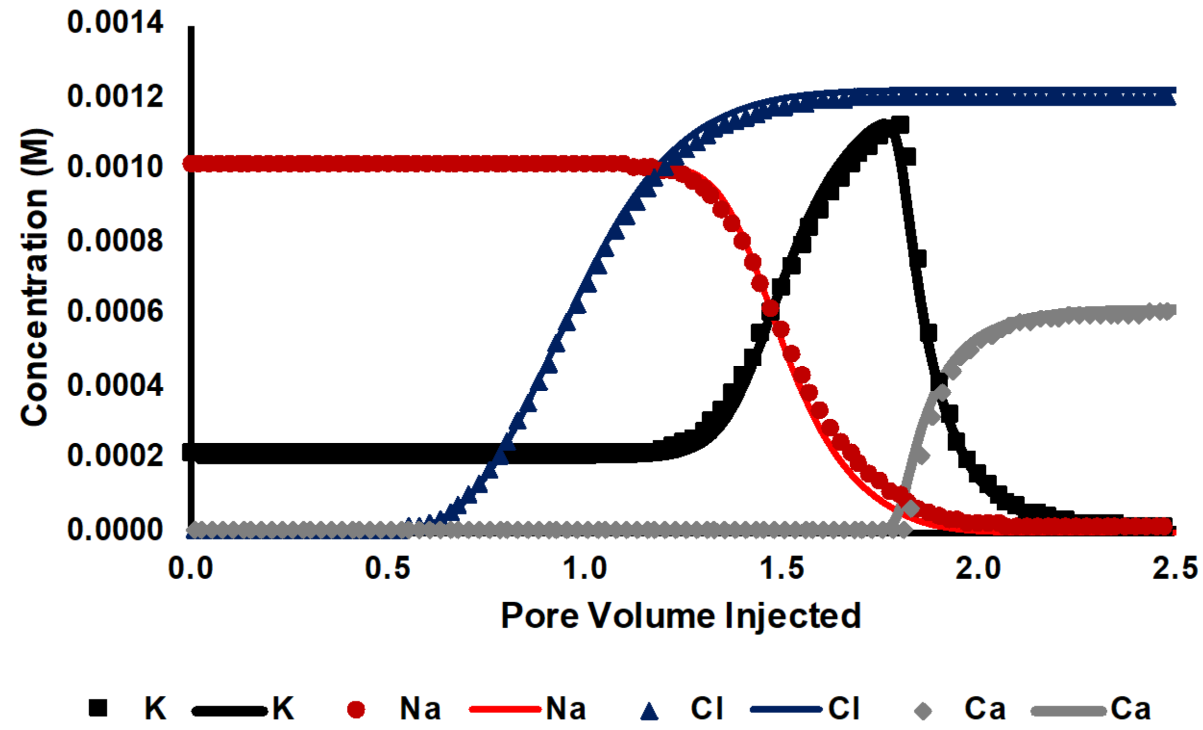
2. Tracer isotope ($^{22}Na^+$ vs Na^+) diffusion due to charge effects[1]
   PHREEQC (symbols), **Osures** (solid) steady-state $^{22}Na^+$ concentration

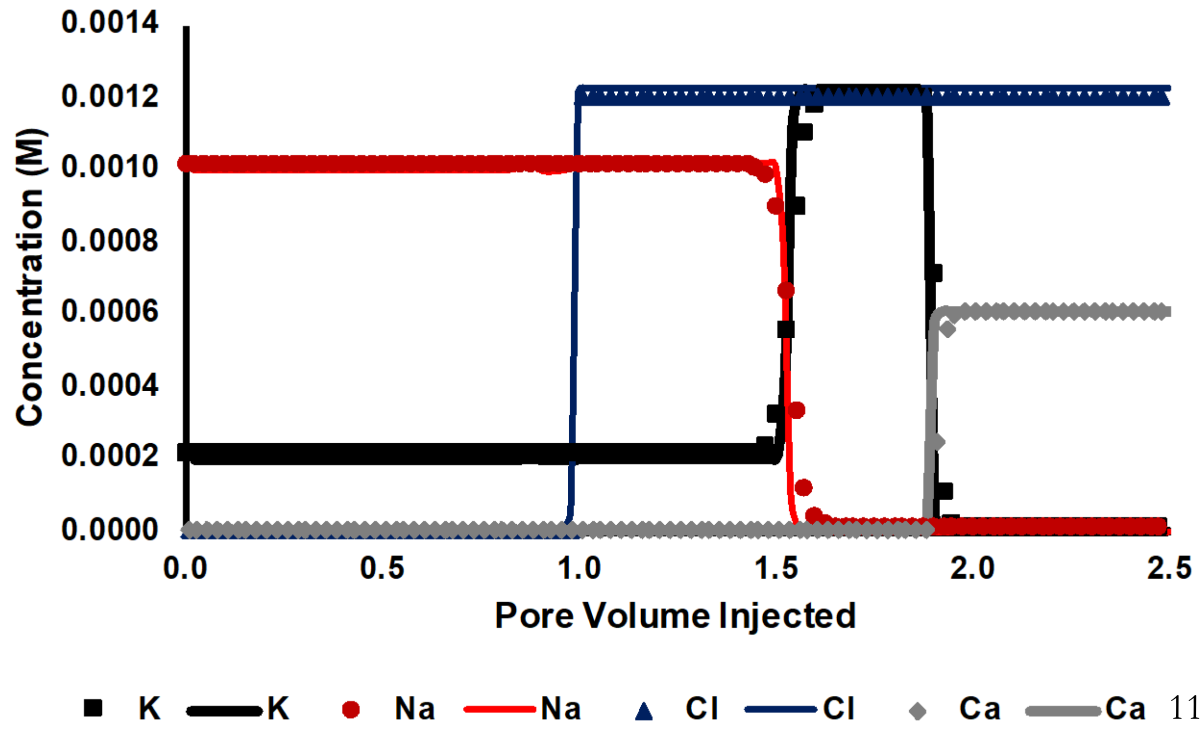


[1]Rasouli, Steefel, Mayer, Rolle; Benchmarks for multicomponent diffusion and electrochemical migration. Comput Geosci (2015)

Benchmarking

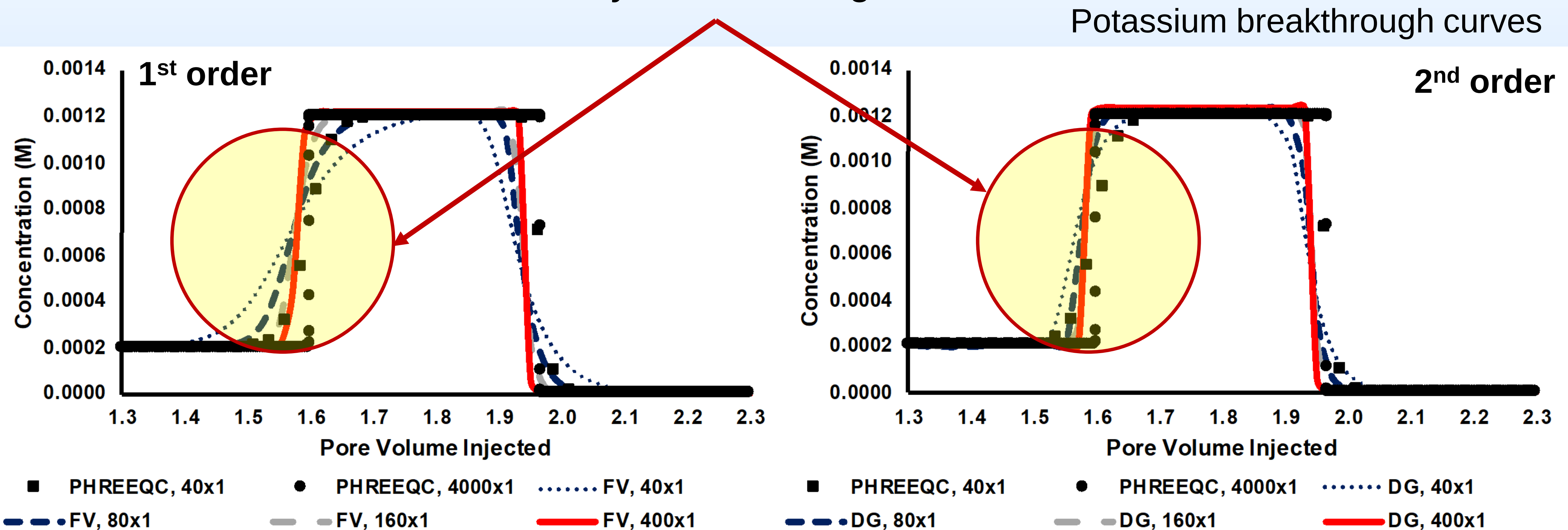
3. Rock-fluid cation exchange column (Ex. 11 PHREEQC manual)
   Advection & dispersion (left), or only advection (right)
   Ca-Cl injected into Na-K-NO_3 solution. Ca^{2+} exchanges with Na^{+} and K^{+}
   PHREEQC (symbols), Osures (solid line)

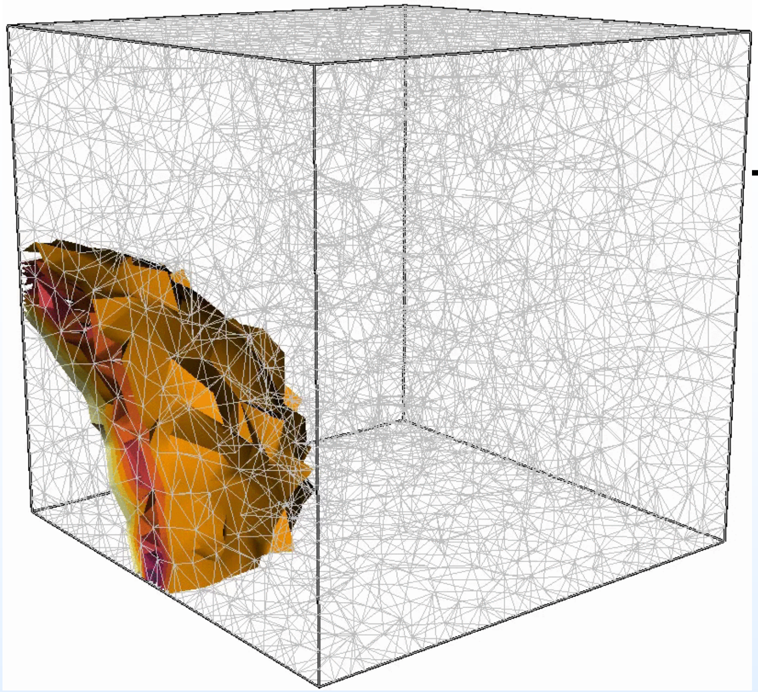




Higher-Order Methods

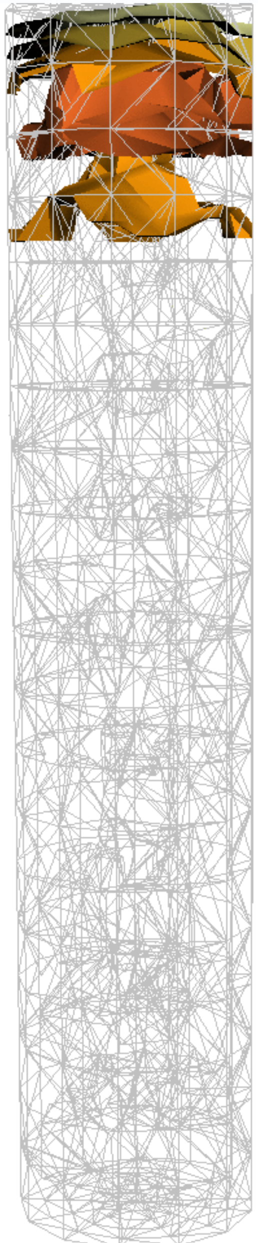
- Mixed (Hybrid) FE method for pressure & velocity field
- Multilinear Discontinuous Galerkin FE for reactive transport
- Accurate velocities and low numerical dispersion
- Unstructured, relatively coarse, 3D grids

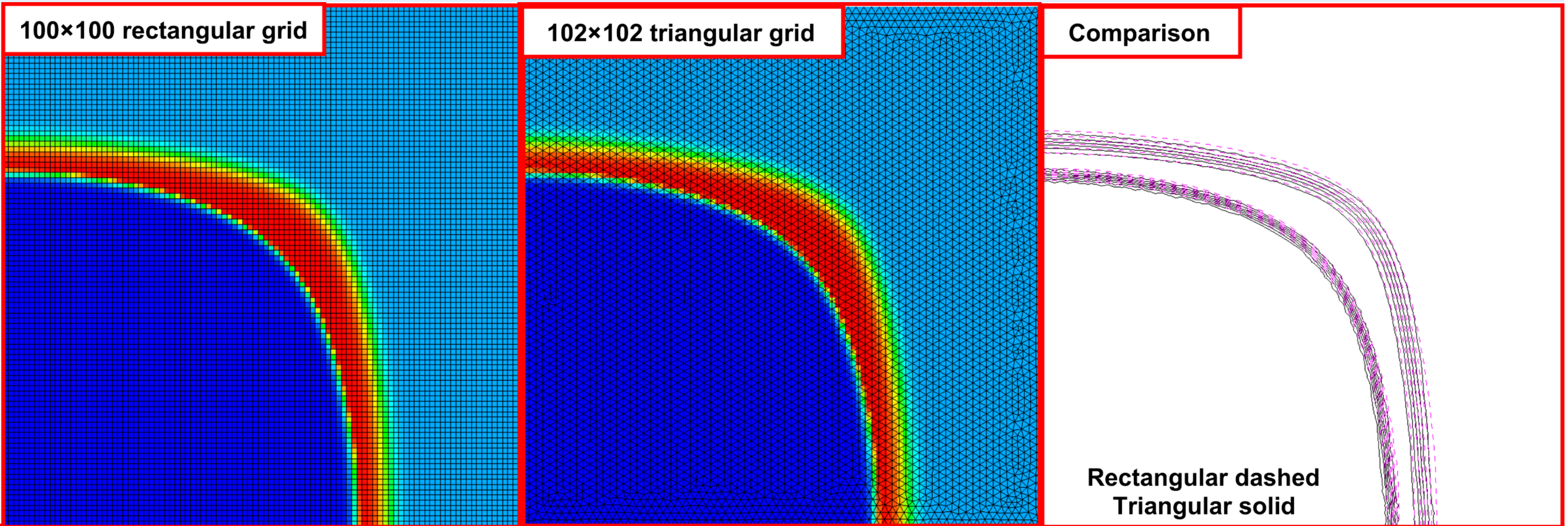




Unstructured Grids

- 2D: Quads & Triangles
- 3D: Tetra- & Hexahedra
- Allows gridding of, e.g., cores and complex geological formations.

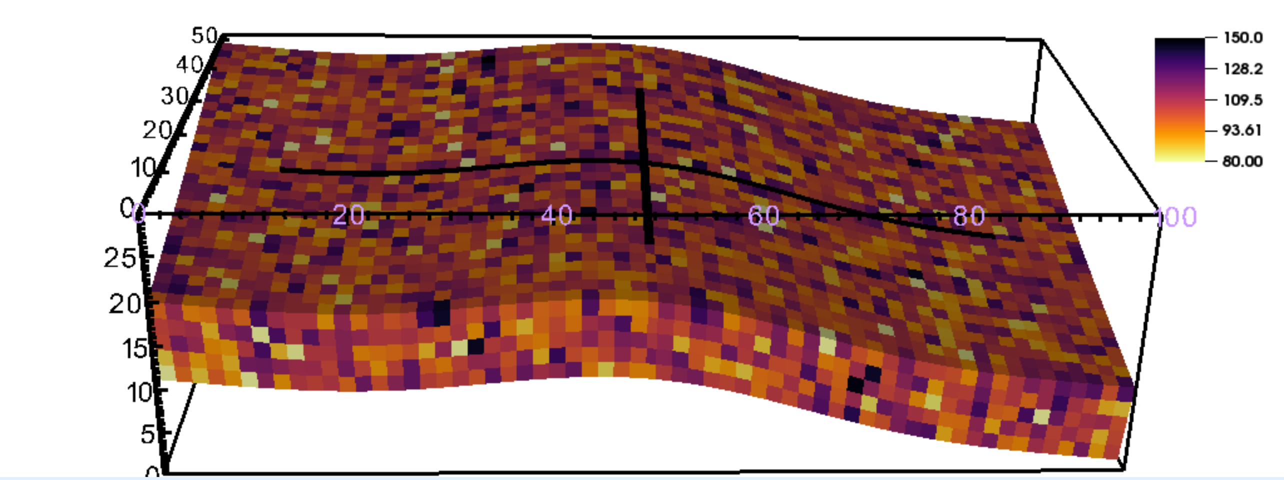




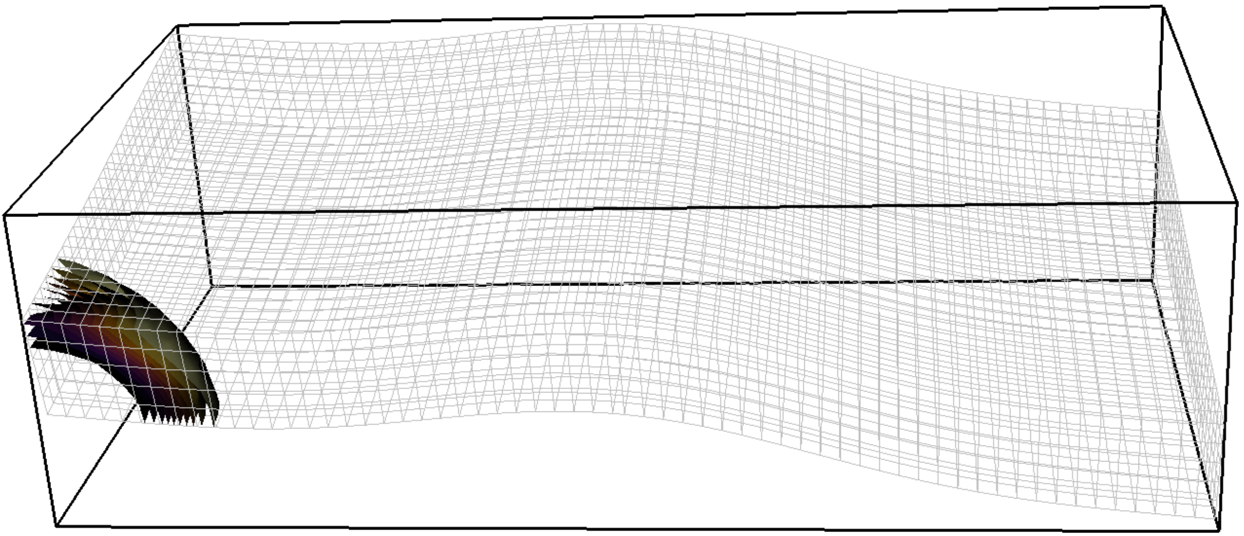
Discrete Fractures

FE discrete fracture example with convection, dispersion, and rock-fluid cation exchange reactions.

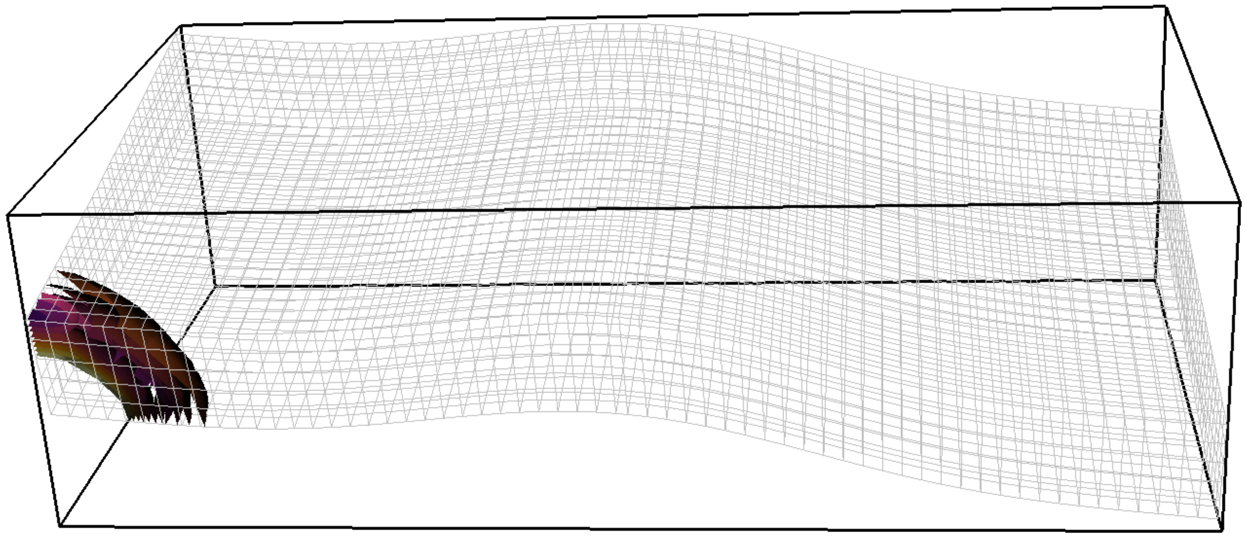
Unstructured grid, **two intersecting fractures** (1 mm aperture, 10^8 mD), log-normal random perms. 75 < k < 150 md.



Chloride (injected)



Potassium (exchange reaction)



Lessons Learned

- Critical uncertainties in modeling/predicting two-phase migration of supercritical CO_2 into brine-saturated formation:
  - Subsurface heterogeneity,
  - Relative permeability & capillary pressure relations: especially facies-dependence.

- Convective mixing of dissolved CO_2 relatively insensitive to multimodal facies heterogeneity when porosity and permeability are correlated. Simple scaling laws in terms of formation/fluid properties apply broadly.

- Rock-fluid reactions likely modest on short time-scales, but may affect long-term storage. Predictions require costly (parallelized) numerical modeling & further research.

Synergy

- Pursuing collaborative opportunities to model CCS projects other than Cranfield.
- In preliminary discussions with MRCSP regarding challenging reef systems.
- Open to other partnerships, incl. future large-scale projects.
- Addressing priority research directions:
  - PRD S-1: Advancing Multiphysics and Multiscale Fluid Flow to Achieve Gton/yr Capacity
  - PRD S-2: Understanding Dynamic Pressure Limits for Gigatonne-scale CO_2 Injection
  - PRD S-6: Improving Characterization of Fault and Fracture Systems

Project Summary (Task 1)

- Completed:
  - Modeling of CO_2, brine, and various tracers at Cranfield.
  - Fundamental analyses of solubility trapping (mixing and spreading of dissolved CO_2).
  - Initial implementation and benchmarking of coupled flow and reactive transport with Osures+iPhreeqc.

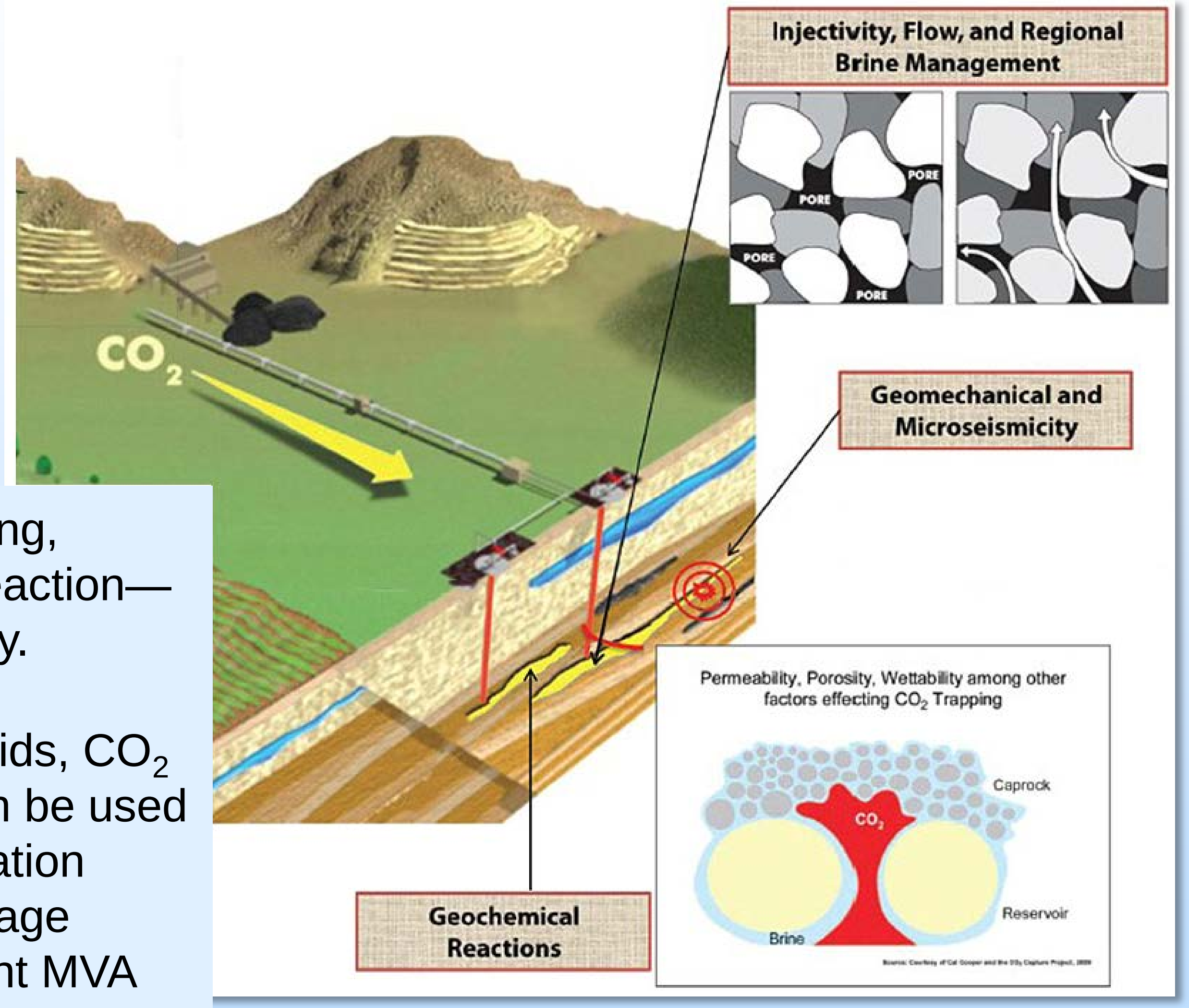
- Ongoing & Future work:
  - Investigation of multiphase flow and reactive transport at Cranfield
  - Technology improvements (specifically parallelization / HCP)
  - Modeling of independent field site(s) to stress-test final developed modeling tools.

APPENDICES

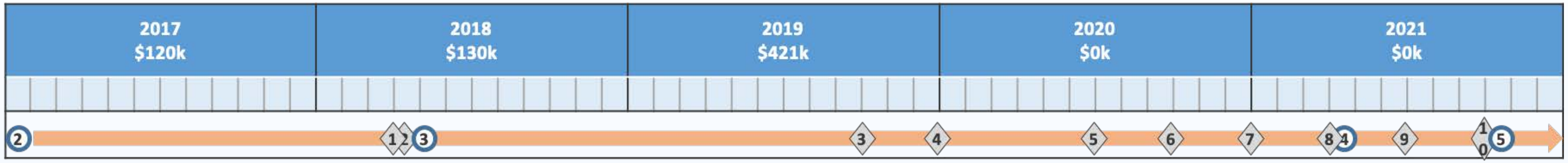
Benefit to Program

Geologic Storage, Simulations, and Risk Assessment

- Provide information on physical and geo-chemical changes in reservoir, ensuring CO_2 storage permanence.
- Facilitate fundamental understanding of processes impacting behavior of fluids—diffusion, dispersion, mixing, advection, capillarity, and reaction—to improve storage efficiency.
- Ground-truth behavior of fluids, CO_2 transport properties that can be used to constrain reservoir simulation models, predicting CO_2 storage capacity & designing efficient MVA programs.

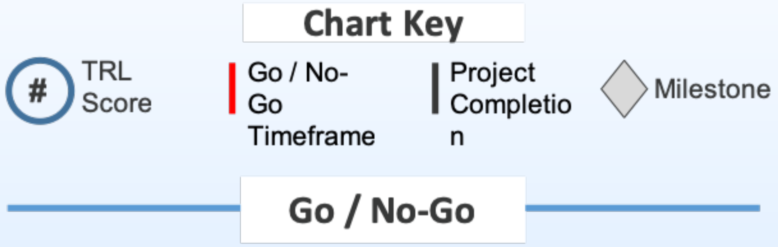


Project Overview



Milestones (2018-2021)

1. Initial incorporation of geochemistry and reactive transport into Osures
2. Report on universal fluid dynamics of gravito-convective mixing
3. Initial transport modeling of aqueous equilibrium reactions
4. Data sharing planned with partner institution(s)
5. Static model developed for a independent CSS project
6. First reactive transport modeling of multiphase brine-CO_2-rock system
7. Modeling of CO_2-brine flow and transport for a field site different from Cranfield DAS
8. Final model of geochemistry and reactive transport at Cranfield
9. Complete CO_2-brine-rock geochemistry and reactive transport incorporated into CSS simulations
10. Final report on Monitoring of Geological CO_2 Sequestration Using Isotopes and Perfluorocarbon Tracers



Impact

Key Accomplishments & Deliverables	Value Delivered
2017 – 2018: • Detailed model of PFT & SF_6 tracer transport at Cranfield site. • Simulated CH_4 and CO_2 transport at Cranfield DAS site. • Prioritized reactive transport processes for simulation. • Developed modeling roadmap "Towards Continuum Reactive Transport Modeling Coupled with Multiphase Compositional Flow in Porous Media."	Most reliable predictive multi-physics modeling tools for geological CO_2 storage to date, as validated by field data from the Cranfield project, • Matching traditional measurements (pressure response, CO_2 breakthrough), • Matching novel PFC tracer data with parts-per-million precision. Tracer data + modeling elucidate CO_2 plume migration (containment) at later times. Universal predictions of dissolution trapping rates & times-scales.

Organization Chart

U.S. DEPARTMENT OF ENERGY | NETL

The University of Tennessee Knoxville

Tommy Phelps

Susan Pfiffner

Oak Ridge National Laboratory

David Graham, PI

The Ohio State University

Joachim Moortgat

David Cole

Postdocs: Soltanian, Zhu, Li

Collaborators:

National Energy Technology Laboratory · Bureau of Economic Geology (John A. and Katherine G. Jackson School of Geosciences) · Berkeley Lab · USGS science for a changing world · Battelle

Gantt Chart

Task	Milestone Description*	Fiscal Year 2019				Fiscal Year 2020				Fiscal Year 2021				Planned Start Date	Planned End Date	Actual Start Date	Actual End Date
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4				
2.1	Thermal desorption system installed on ORNL's gas chromatography system													2/19	4/19	2/19	
2.1	Sorbent selected for PFT-hydrocarbon experiments													3/19	6/19		
1.1	Initial transport modeling of aqueous equilibrium reactions with Osures+iPhreeqc													3/18	9/19	3/18	
1.2	Data sharing planned with partner institution(s) for future modeling of a CCS project independent of the Cranfield DAS													3/19	12/19		
2.1	Validation of PFT sorbent sampling method in hydrocarbon matrices													7/19	12/19		
2.1	Best practices identified for PFT sampling in hydrocarbon-rich environments													9/19	3/20		
1.2	Static model developed for a modeling benchmark study of an independent CSS project													7/19	6/20		
1.1	First demonstrations of reactive transport modeling of the multiphase brine-CO2-rock system using higher-order accurate methods													7/19	9/20		
1.2	Modeling of CO2-brine flow and transport for a field site different from Cranfield DAS													1/20	12/20		
1.1	Final model of geochemistry and reactive transport at Cranfield													7/20	3/21		
1.1	Complete CO2-brine-rock geochemistry and reactive transport incorporated into CSS simulations													10/20	6/21		
3	Final report on Monitoring of Geological CO2 Sequestration Using Isotopes and Perfluorocarbon Tracers													1/20	9/21		

Task 1 - Bibliography I/II

1. **Amooie, M.A., Soltanian, M.R., and Moortgat, J.,** “Solutal Convection in Porous Media: Comparison Between Boundary Conditions of Constant Concentration and Constant Flux”, Physical Review E. (2019), 98(3), 033118. doi:10.1103/PhysRevE.98.033118.

2. **Soltanian, M.R., Amooie, M.A., Cole, D.R., Graham, D., Pfiffner, S., Phelps, T., and Moortgat, J.**, “Transport of Perfluorocarbon Tracers in the Cranfield Geological Carbon Sequestration Project”, Greenhouse Gases, Science and Technology (2018), 8(4), 650–671. doi:10.1002/ghg.1786.

3. Dai, Z., Zhang, Y, Stauffer, P.H., Bielicki, J.M., **Amooie, M.A**., Zhang, M. Yang, C., Zou, Y., Ampomah, W., Xiao, T., Jia, W., Middleton, R.S., Zhang, W., Sun, Y., **Moortgat, J., and Soltanian, M.R**., “Heterogeneity-assisted carbon dioxide storage in marine sediments”, Applied Energy (2018), 225, 876–883. doi:10.1016/j.apenergy.2018.05.038.

4. **Moortgat, J.,** “Reservoir Simulation with the Cubic Plus (Cross-) Association Equation of State for Water, CO2, Hydrocarbons, and Tracers”, Advances in Water Resources (2018), 114(C), 29-44. doi:10.1016/j.advwatres.2018.02.004.

5. **Soltanian, M.R.,** Dai, Z., Yang, C., **Amooie, M.A., Moortgat, J.**, “Multicomponent Competitive Monovalent Cation Exchange in Hierarchical Porous Media with Multimodal Reactive Mineral Facies”. Stochastic Environmental Research and Risk Assessment (2018), 32(1), 295–310. doi:10.1007/s00477-017-1379-y.

6. **Moortgat, J.,** Schwartz, F., and Darrah, T.H., “Numerical Modeling of Methane Leakage in Fractured Tight Formations”, Groundwater (2018), 56(2). doi:10.1111/gwat.12630.

7. **Soltanian, M.R., Amooie, M.A., Cole, D.R.,** Darrah, T.H., **Graham, D., Pfiffner, S., Phelps, T., and Moortgat, J.**, “Impacts of Methane on Carbon Dioxide Storage in Brine Formations”, Groundwater (2018), 56(2). doi:10.1111/gwat.12633.

Task 1 - Bibliography II/II

8. **Amooie, M.A., Soltanian, M.R.,** Xiong, F., Dai, Z., **Moortgat, J.**, "Mixing and Spreading of Multiphase Fluids in Heterogeneous Bimodal Porous Media", Geomechanics and Geophysics for Geo-Energy and Geo-Resources (2017), 3(3), 225–244. doi:10.1007/s40948-017-0060-8.

9. **Soltanian, M.R.,** Sun, A., Dai, Z., "Reactive Transport in a Complex Heterogeneous Alluvial Aquifer of Fortymile Wash, Nevada", Chemosphere (2017), 179, 379-386.

10. **Soltanian, M.R., Amooie, M.A**., Gershenzon, N., Dai, Z., Ritzi, R., Xiong F., **Cole, D.R**., and **Moortgat, J**., "Dissolution Trapping of Carbon Dioxide in Heterogeneous Aquifers", Environmental Science and Technology (2017), 51(13), 7732–7741. doi:10.1021/acs.est.7b01540.

11. **Amooie, M.A., Soltanian, M.R., Moortgat, J**., "Hydro-Thermodynamic Mixing of Fluids Across Phases in Porous Media". Geophysical Research Letters (2017), 44(8), 3624-3634. doi:10.1002/2016GL072491.

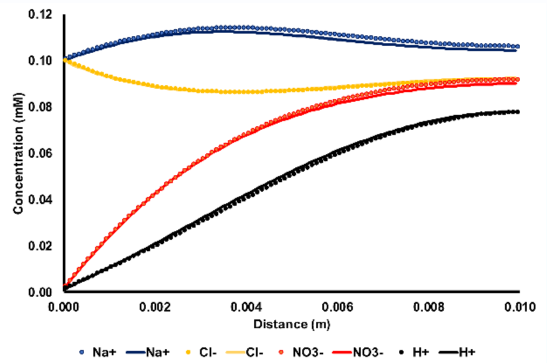
12. **Soltanian M.R., Amooie, M.A**., Dai, Z., **Cole, D**., and **Moortgat, J.,** "Critical Dynamics of Gravito-Convective Mixing in Geological Carbon Sequestration". Scientific Reports (2016), 6, 35921.

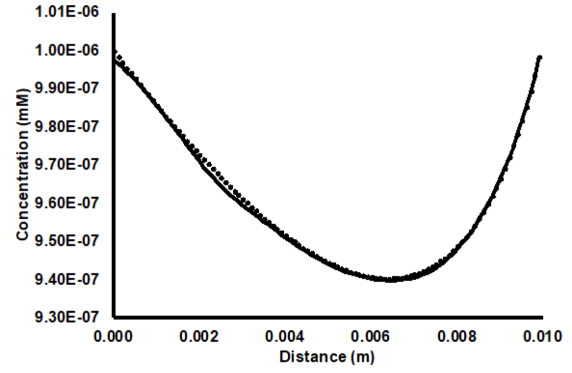
13. **Soltanian M.R**., **Amooie, M.A**., **Cole, D.R**., **Graham, D.E.,** Hosseini, S.A., Hovorka, S., **Pfiffner, S.M., Phelps**, **T.J., Moortgat, J**., "Simulating the Cranfield Geological Carbon Sequestration Project with High-Resolution Static Models and an Accurate Equation of State" International Journal of Greenhouse Gas Control (2016), 54, Part 1, 282–296, doi:10.1016/j.ijggc.2016.10.002.

14. **Moortgat, J., Amooie, M.A. and Soltanian M.R.:** "Implicit Finite Volume and Discontinuous Galerkin Methods for Multicomponent Flow in Unstructured 3D Fractured Porous Media," Advances in Water Resources (2016), 96, 389–404, doi:10.1016/j.advwatres.2016.08.007.

Benchmarking

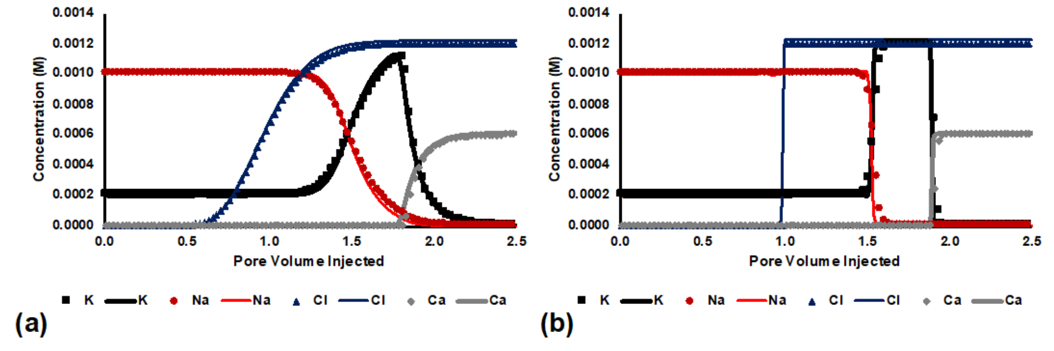
1. Electrochemical migration (Nernst-Planck diffusion[1]) of Na^+, Cl^-, H^+, NO_3^-. Modeled with CrunchFlow, MIN3P, PHREEQC (symbols), **Osures** (solid).





2. Tracer isotope ($^{22}Na^+$ vs Na^+) diffusion due to charge effects[1] PHREEQC (symbols), **Osures** (solid) steady-state $^{22}Na^+$ concentration

3. Rock-fluid cation exchange column (Ex. 11 PHREEQC manual), convection & diffusion.



[1]Rasouli, Steefel, Mayer, Rolle; Benchmarks for multicomponent diffusion and electrochemical migration. Comput Geosci 19(3), 523–533 (2015)