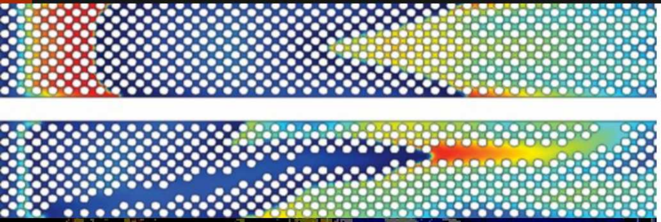
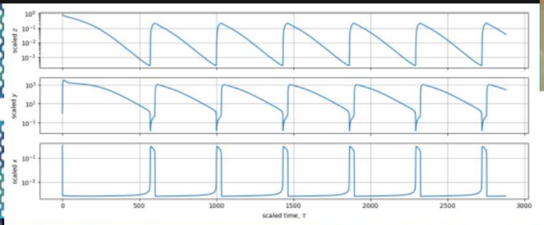
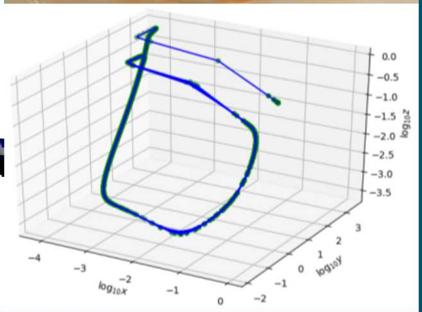
SAND2019-3726C

Nonlinear Tracers and *In Situ* Computing: Subsurface Sensing with Chemical Waves







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Overview and Acknowledgements

- Background
- Microfluidic Experiments
- CFD Numerical Experiments
- Examples:
  - -characterization
  - -fracture aper. “mapping”
  - -detection of contaminants
- Further Musings
- Conclusions

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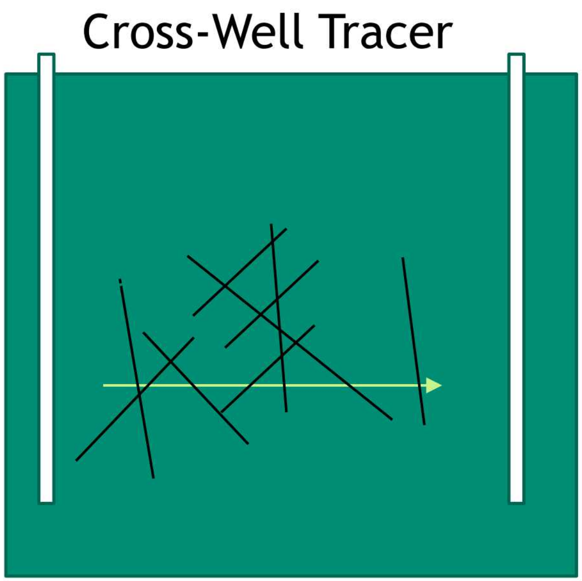
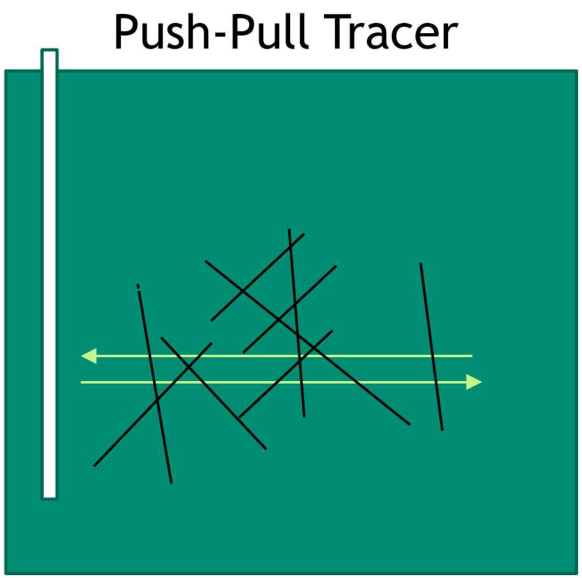
Subsurface Sensing with Chemical Waves

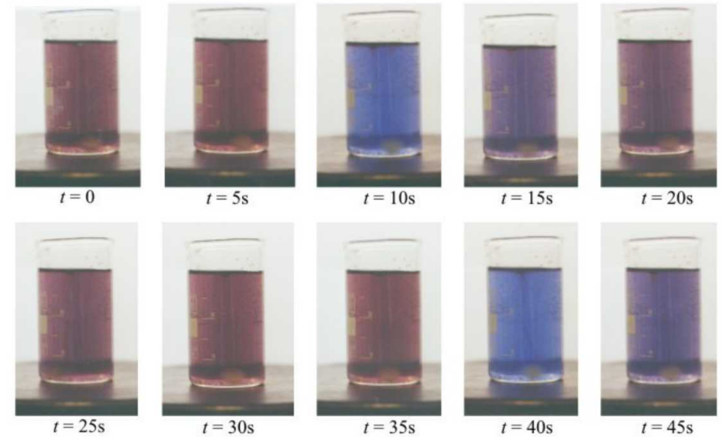
- **Central premise**: Chemical kinetics systems with multiple stationary states coupled to transport can support ***chemical waves*** with the ability to provide information on spatial networks through which they propagate
- Chemical waves are self-sustaining disturbances in chemical or other variables that propagate over distance with or without attenuation (Ortoleva, 1992) arising from ***nonlinear coupling*** of chemical reaction and transport under far-from equilibrium conditions (Nicolis and Prigogine, 1977).
- Use of chemical waves for subsurface sensing are termed here "***nonlinear tracers***" to discern from usual linear tracers, such as isotopes, conservative tracers such as Cl or Br, temperature, etc.





Belousov-Zhabotinsky Reaction

- Canonical oscillatory reaction is the oft-studied Belousov-Zhabotinsky (BZ) reaction
- Organic substrate (malonic acid) oxidized by bromate in acidic solution with metal (Fe) catalyst
- Complex kinetic steps. A simple model is the *Oregonator* (Field et al., 1972) in which the autocatalytic step is made clear (X is $HBrO_2$, Y is Br^-, and Fe^{3+} or other catalyst; A and P are “pool” concentrations):



Belousov-Zhabotinsky reaction in stirred beaker and petri dish, showing oscillations in blue and red regions corresponding to Fe oxidation state (photo from Michael C. Rogers and Stephen Morris, University of Toronto, https://en.wikipedia.org/wiki/Belousov%E2%80%93Zhabotinsky_reaction

$$A + Y \rightarrow X + P$$

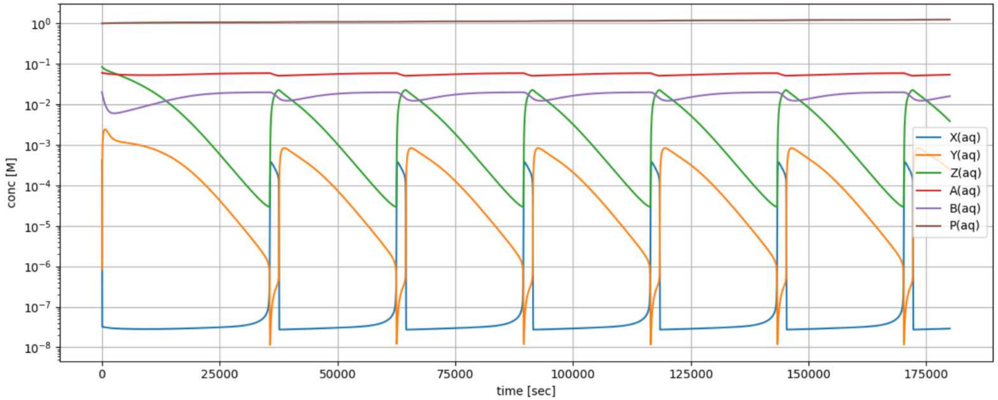
$$X + Y \rightarrow 2P$$

$$A + X \rightarrow 2X + Z^*$$

$$2X \rightarrow A + P$$

$$Z \rightarrow f\,Y$$

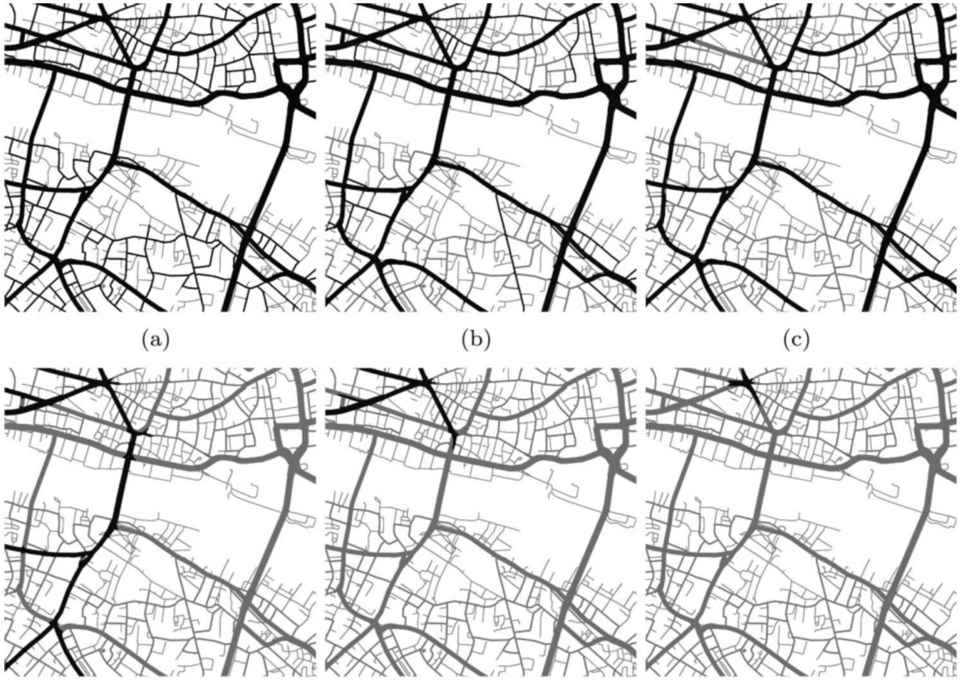
*autocatalytic step



Numerical solution of *Oregonator* reaction scheme using PFLOTRAN

Unconventional Computing Examples

- "liquid chemical computing": chemical waves interacting with a geometrical medium can be used as chemical switches (Rossler, 1974); logic gates (Hjelmfelt and Ross, 1995); chemical neural networks and Turing machines (Hjelmfelt et al., 1991); and chemical clocks (Winfree, 1982).
- Generally, chemical kinetics systems with multiple stationary states coupled to transport can support chemical waves with the ability to provide information on spatial networks through which they propagate (Hjelmfelt et al., 1993; Steinbeck et al., 1996).



Tunable BZ-like dynamics propagate top to bottom thru street network according to size (from Adamatsky et al., 2018)

CFD Modeling: “Skeleton Model” of CHD-Br-Fe System

$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr$ (R2)

$Br^- + BrO_3^- + 2H^+ \rightarrow HBrO_2 + 2HOBr$ (R3)

$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+$ (R4)

$HBrO_2 + BrO3^- + H^+ = 2BrO_2^* + H_2O$ (R5)

$H_2Q + 2BrO_2^* \rightarrow 2HBrO_2 + Q$ (R6a)

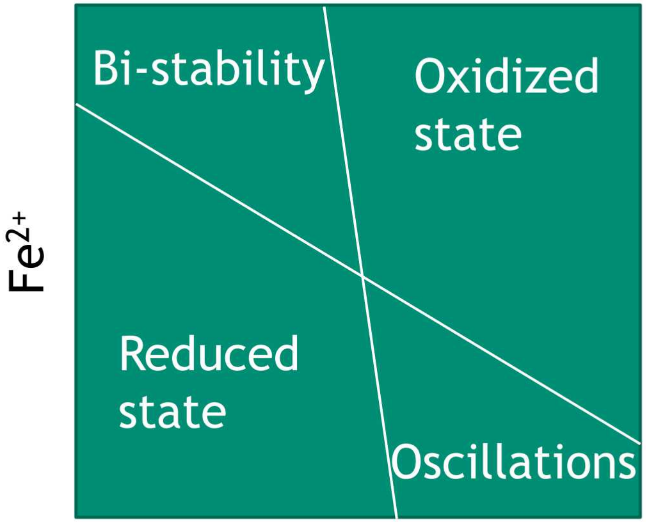
$Fe^{2+} + BrO_2^* + H^+ = Fe^{3+} + HBrO_2$ (R6b)

$BrCHD \rightarrow f\ H_2Q + Br^- + H^+$ (R9)

$H_2Q + BrO_3^- + H^+ \rightarrow HBrO_2 + Q + H_2O$ (R13)

$2\ Fe^{3+} + BrCHD \rightarrow H_2Q + Br^- + 2\ Fe^{2+} +.....$ (R16)

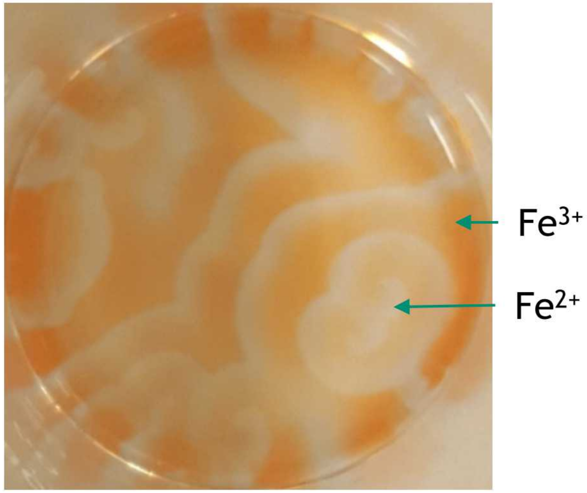
- Reaction network from Szalai et al., 2002; 2003
- Uses 1,4-Cyclohexandione (CHD) as organic substrate (CO_2 generated remains in solution)
- Similar autocatalytic step as original BZ



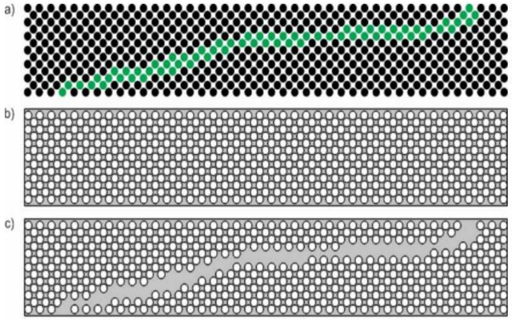
Simplified chemical system and behavior diagram from Szalai et al. 2003, J. Phys. Chem 107

Microfluidics Experiments

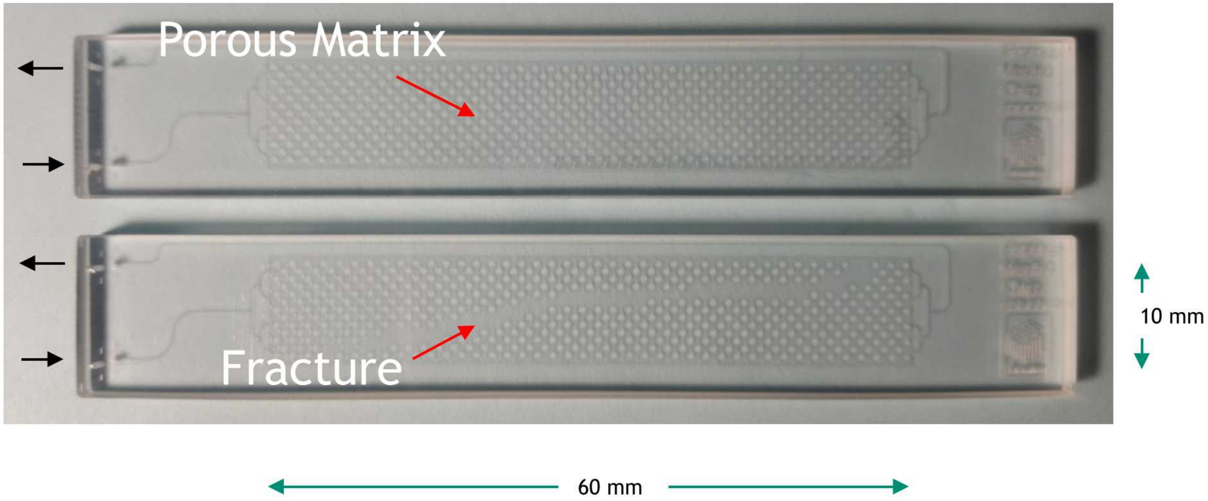
- Two glass microfluid cells are used to examine excitability of BZ media to advection in porous media
- Use CHD as organic substrate to avoid bubbles in microfluidic cells
- Influent fed from well mixed BZ media



Chemical waves in CHD-Br-Fe system in beaker

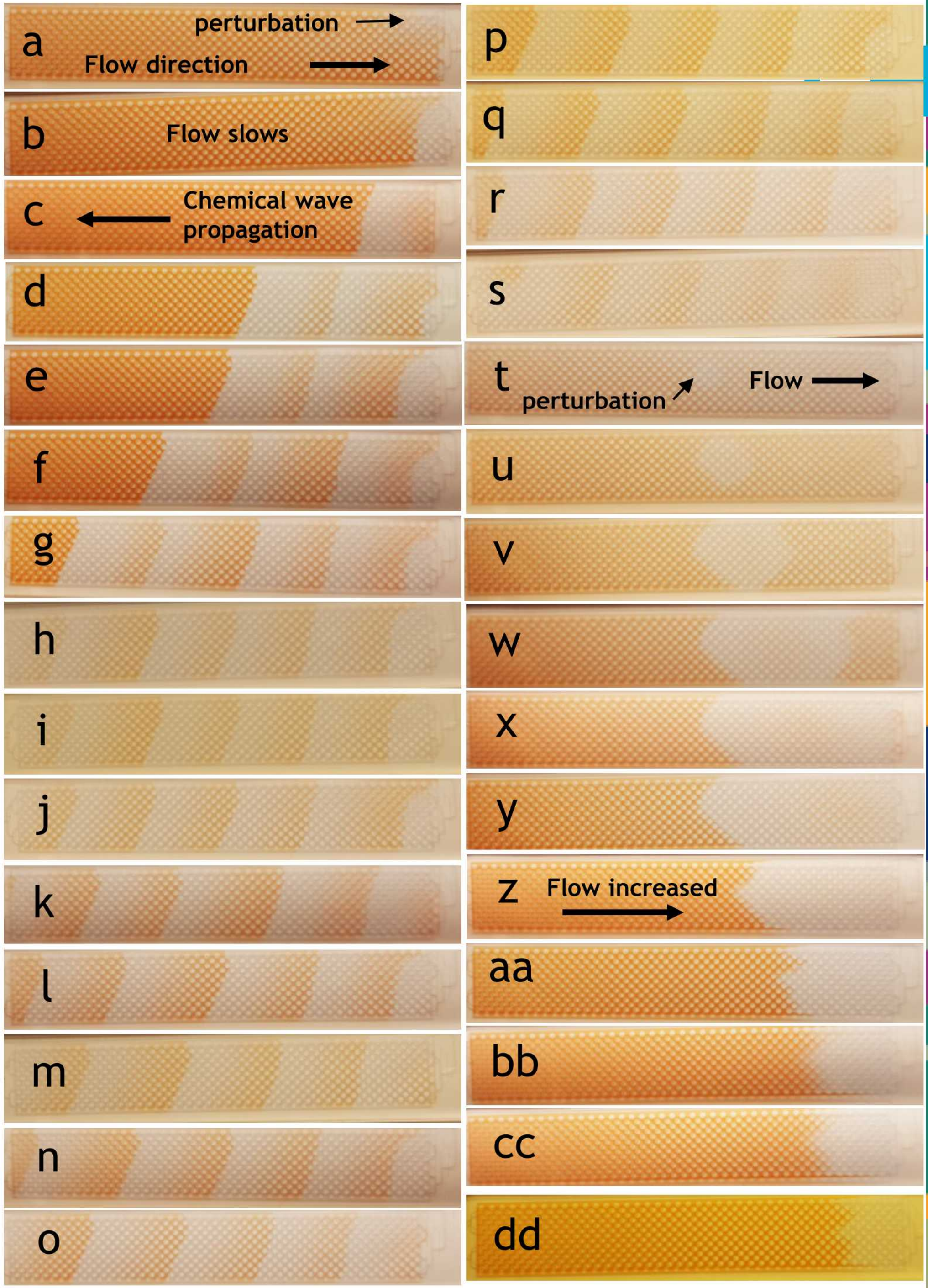


Schematics of micromodel columns in a 60 mm long by 10 mm tall domain. Black and green circles represent the full regular packing of columns. Green represents columns to be removed for fracture modeling.



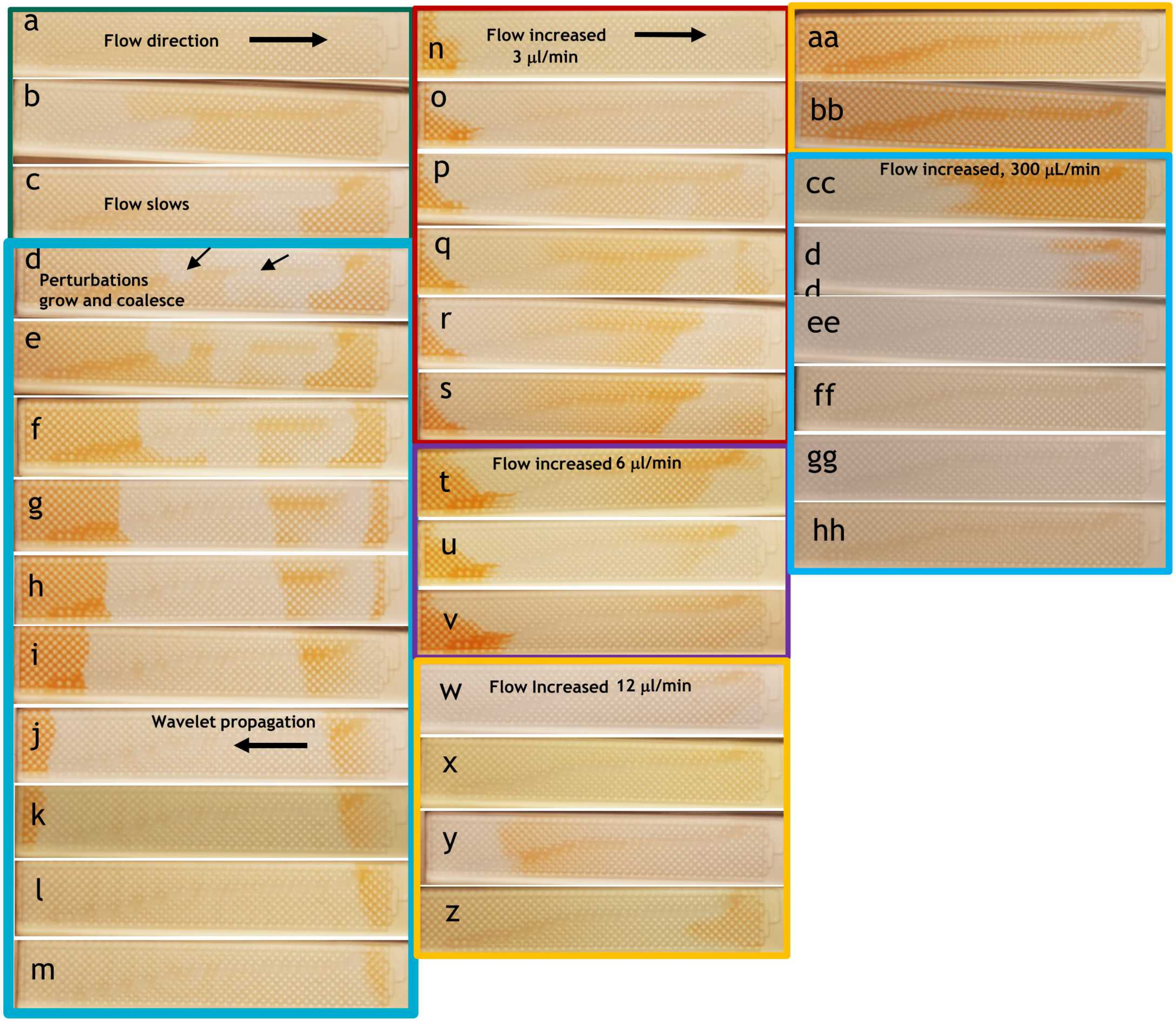
Microfluidics Results

- Volumetric flow uses Optos Eldex HPLC pump
- Flow rate ranges from 1 to 0.1 microliters/s
- Flow rate is stepped down and stepped up
- Variety of chemical wave propagation observed



Microfluidics Results (cont'd)

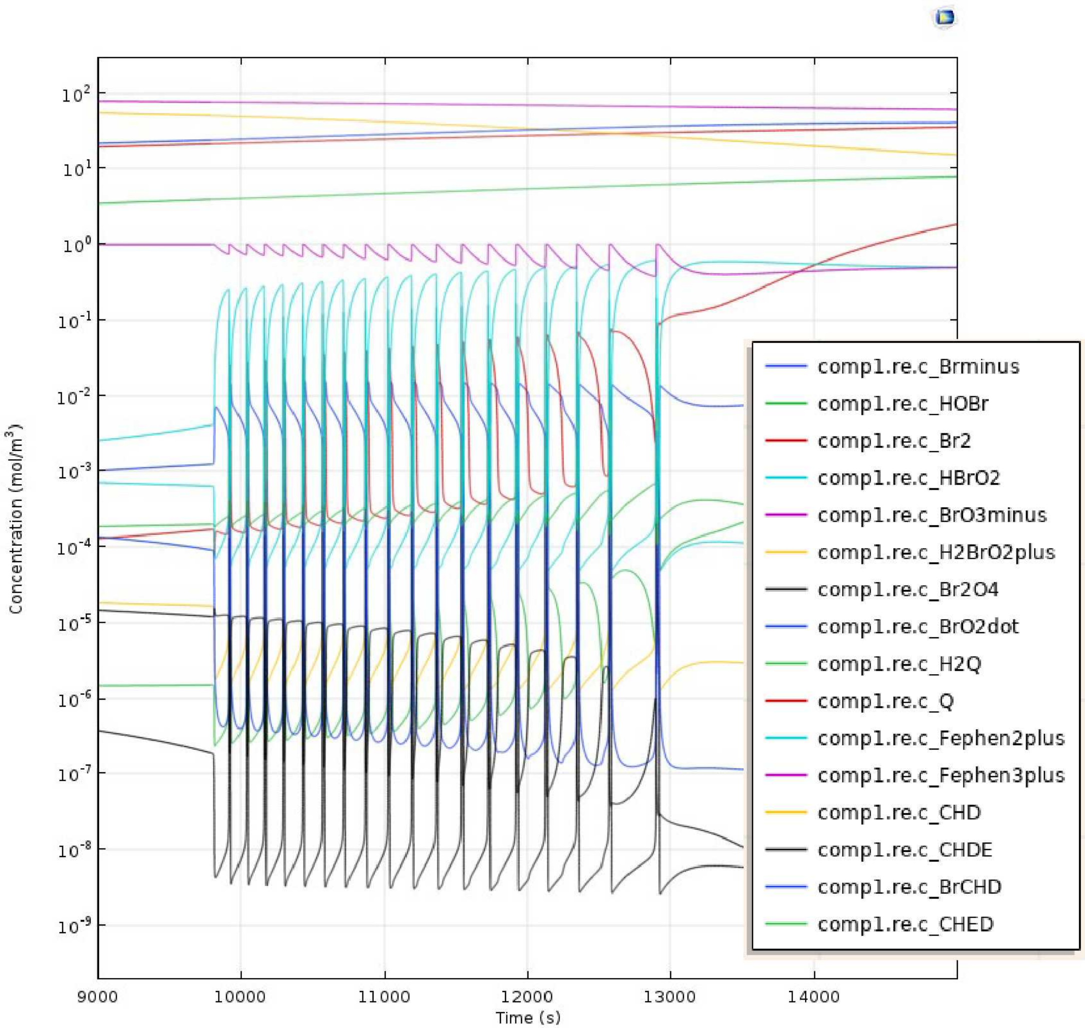
- Examples with "fracture
- Wave generation and propagation vary from previous example
- Chemical wave tracers could be used to characterize porous media
- Sensitivity to advection velocity



Summary of Experimental Observations

- Spatio-temporal chemical waves will advance from spatial perturbations, but will not initiate in an initially spatially homogeneous concentration field
- Wave trains of advancing zones of alternating redox state are initiated and sustained, with period/wavelength sensitive to the properties of the porous media
- Wave trains are sensitive to flow conditions. In the absence of flow, waves advance at rates faster than diffusion rates through the cells. In low flow conditions, waves can remain spatially stagnant or even migrate against the advective gradient
- At higher rates of flow, chemical wave trains can be swept along at rates commensurate with the advective velocity, and the instability leading the spatio-temporal oscillatory behavior is dampened
- At sufficiently high advective flow rates, any spatial variability is wiped out, but the pore solution can still exhibit chemical clock behavior in a manner uninfluenced by the porous texture

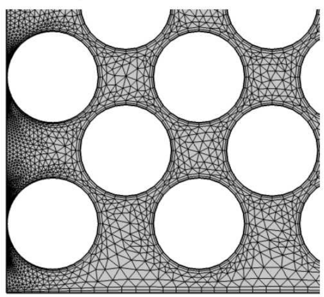
CHD-Br-Fe System: Numerical Examples



- Model of Salazai et al., (2002) with complex kinetics involving ~49 steps
- Solution of a simpler 19-step "skeleton model" in batch mode shown at left, a good approximation of the Salazai et al. (2002) experimental behavior
- ~20 minute induction time required, after which the system develops complex oscillations

Computational Fluid Dynamics Modeling

- Coupled Navier-Stokes equations with species continuity equations (keeping inertial terms) and assuming incompressible flow
- Shallow channel approximation for microfluidic cell thickness
- Nonlinearly coupled reaction network with (pseudo) mass action kinetics
- Triangular mesh:



$$\rho \frac{\partial \boldsymbol{u}}{\partial t} + \rho(\boldsymbol{u} \cdot \nabla)\boldsymbol{u} = \nabla \cdot [-p\boldsymbol{I} + \boldsymbol{K}] - \frac{\mu \boldsymbol{u}}{d_z^2}$$

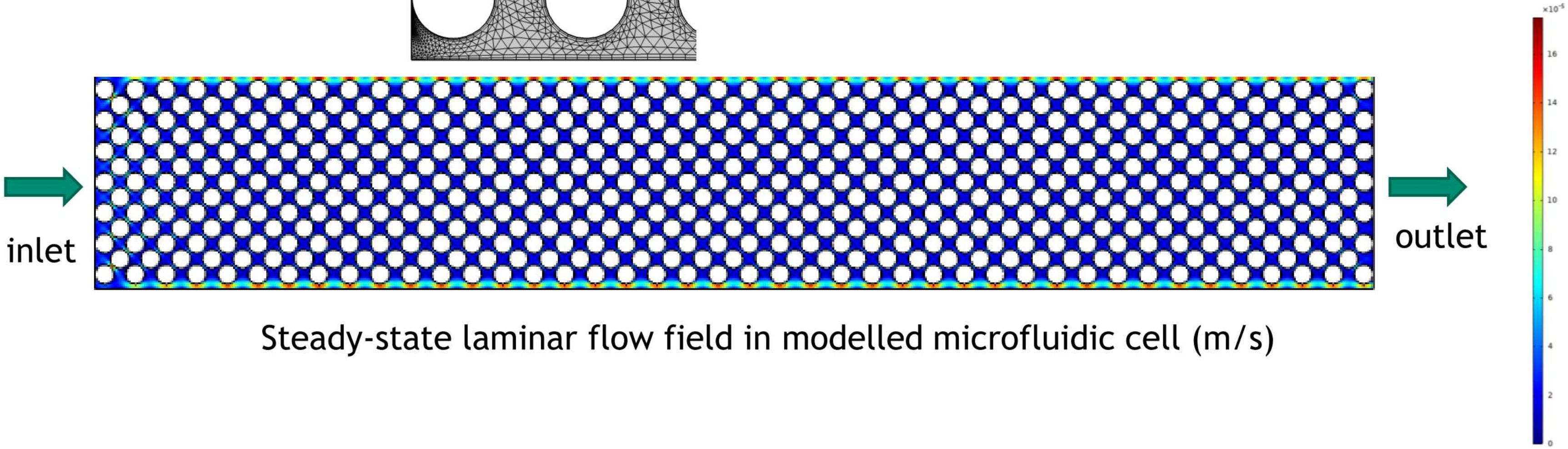
$$\frac{\partial c_i}{\partial t} + \nabla \cdot J_i + \boldsymbol{u} \cdot \nabla c_i = R_i$$

$$\rho \nabla \cdot \boldsymbol{u} = 0 \qquad \boldsymbol{K} = \mu\left(\nabla \boldsymbol{u} + (\nabla \boldsymbol{u}))^T\right)$$

$$J_i = -D_i \nabla c_i$$

$$R_i = \vartheta_i r \qquad r_j = k_j^f \prod_i c_i^{-\vartheta_{ij}}$$

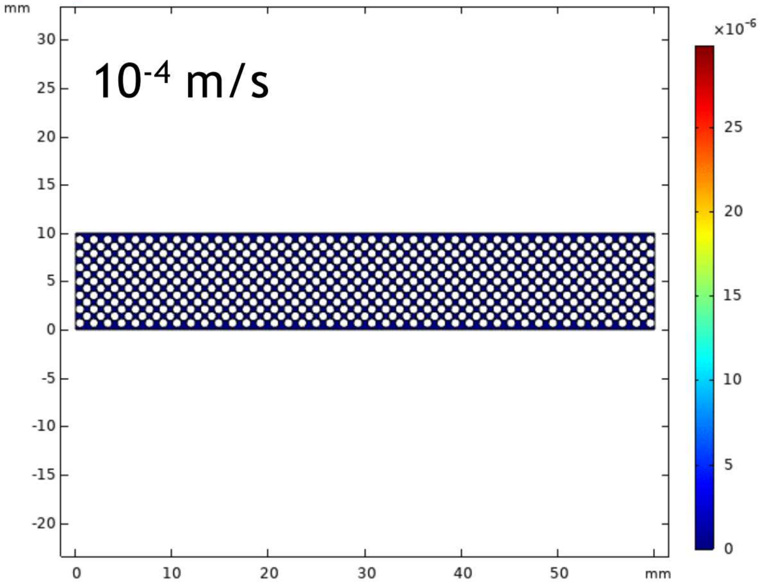
inlet



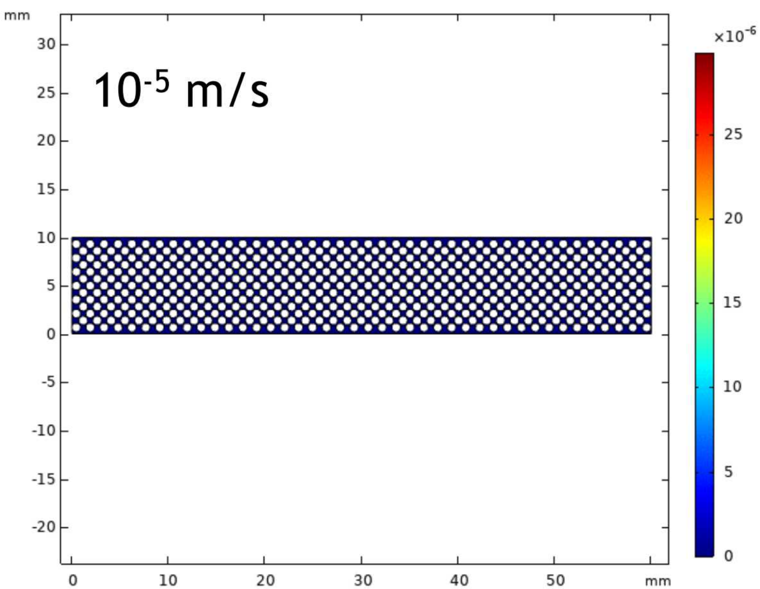
outlet

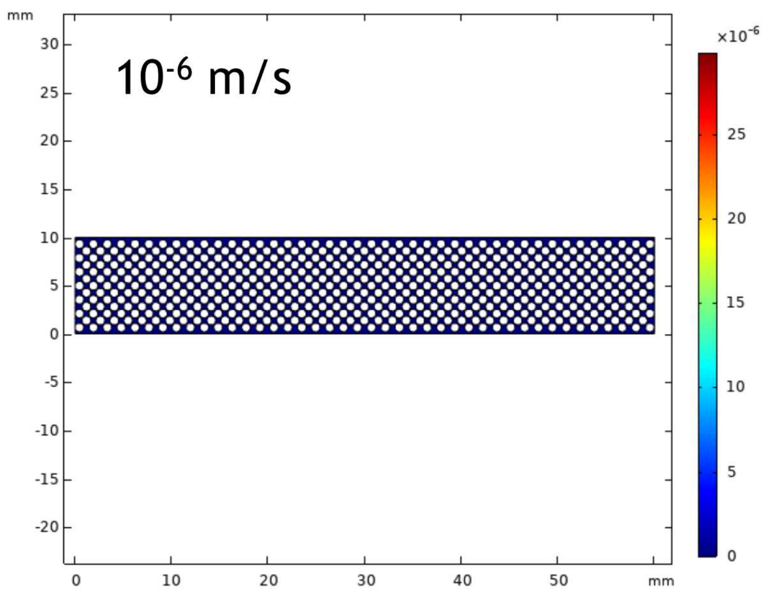
Steady-state laminar flow field in modelled microfluidic cell (m/s)

CFD Animations of Full CHD-Br-Fe: Advective gradient



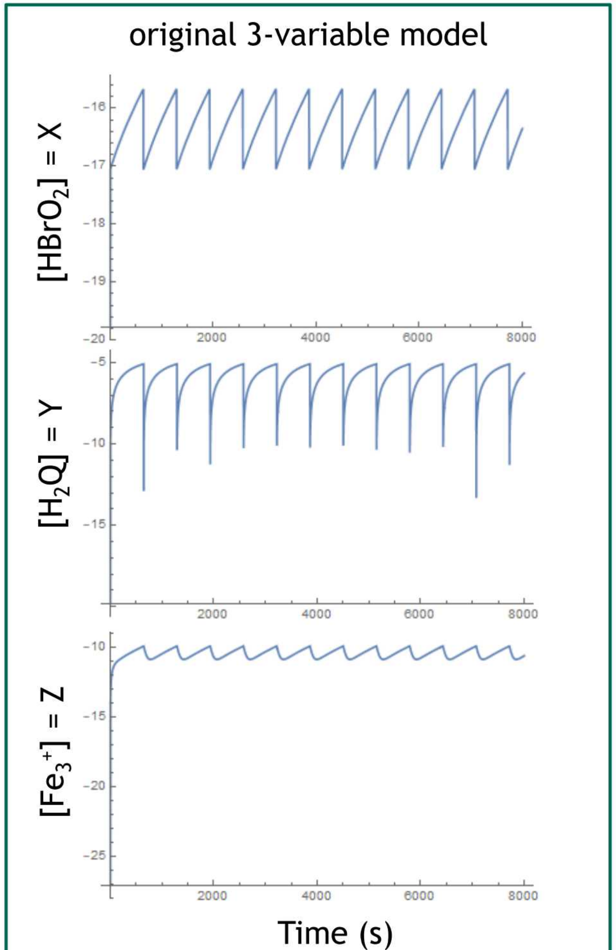
- Waves influenced by advection
- >10^{-4} m/s- wipes out organized wave
- 10^{-4} m/s: standing wave
- 10^{-5} m/s: waves propagating upstream and downstream
- 10^{-6} m/s: wave propagating against advective gradient

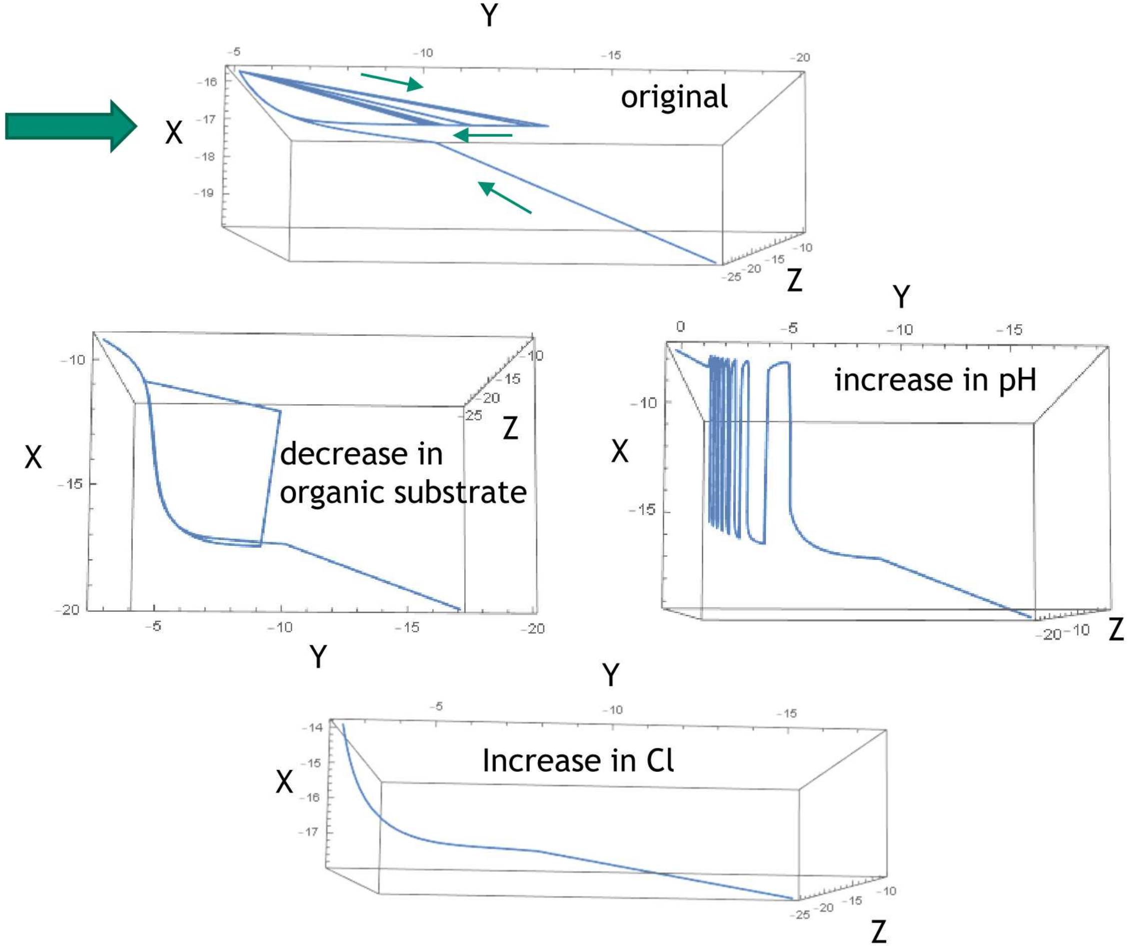




Applications – Contaminant Detection

- Reduce CHD-Br-Fe reaction network to Oregonator-like dynamics
- Solve system in 1D moving reference frame
- Perturb kinetics and examine phase space behavior
- Quite sensitive to environmental variations in pH, Cl-, organic substrate





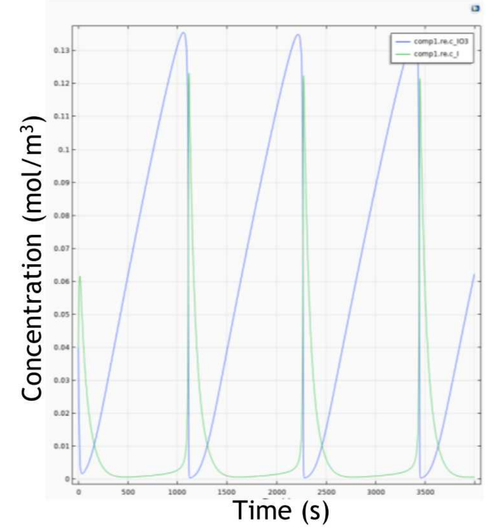
Applications: Other Chemical Systems

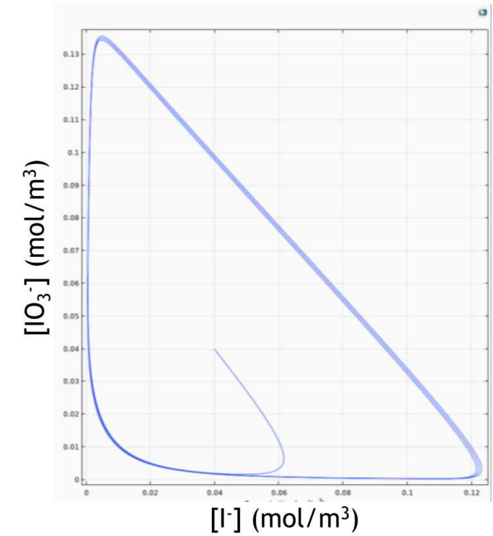
$$NaIO_3 \rightarrow Na^+ + IO_3^-, \quad k_1 = 1.67e\text{-}5$$

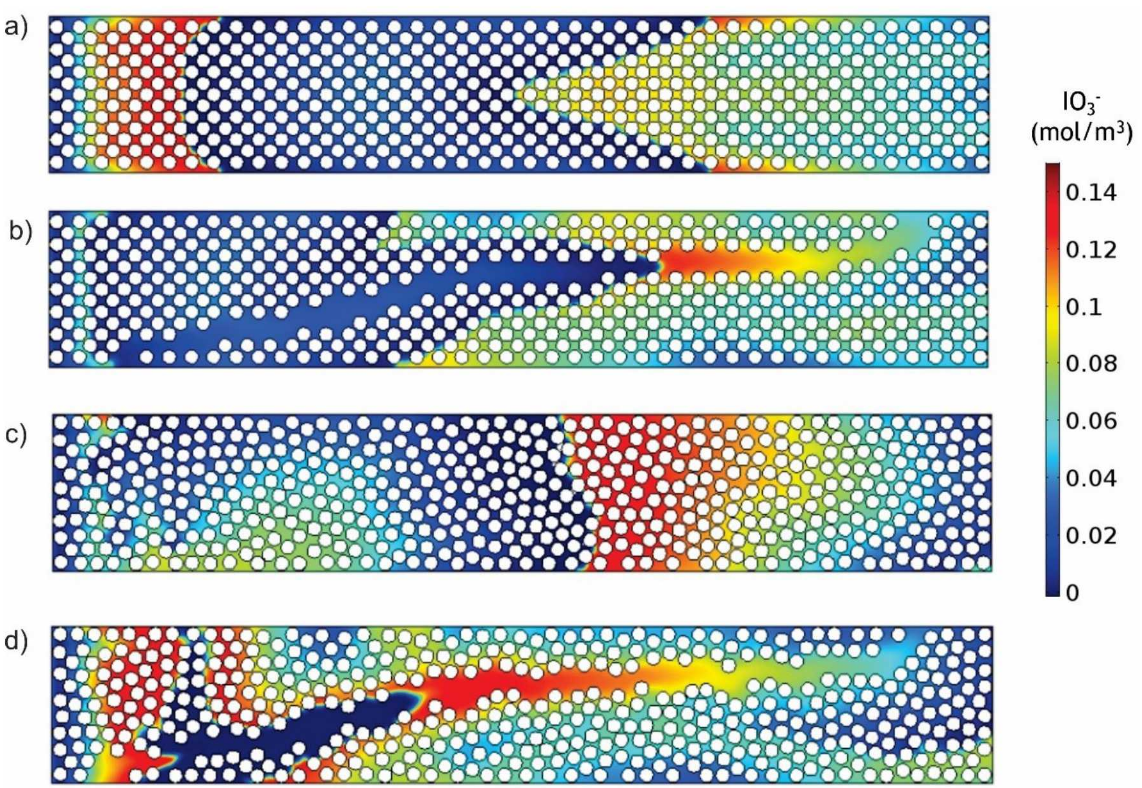
$$IO_3^- \rightarrow I^- + P1, \quad k_2 = 1.67e\text{-}4$$

$$IO_3^- + 2I^- \rightarrow 3I^- + P2, \quad k_3 = 41.7$$

$$I^- \rightarrow 0.5I_2, \quad k_4 = 1.67e\text{-}2$$





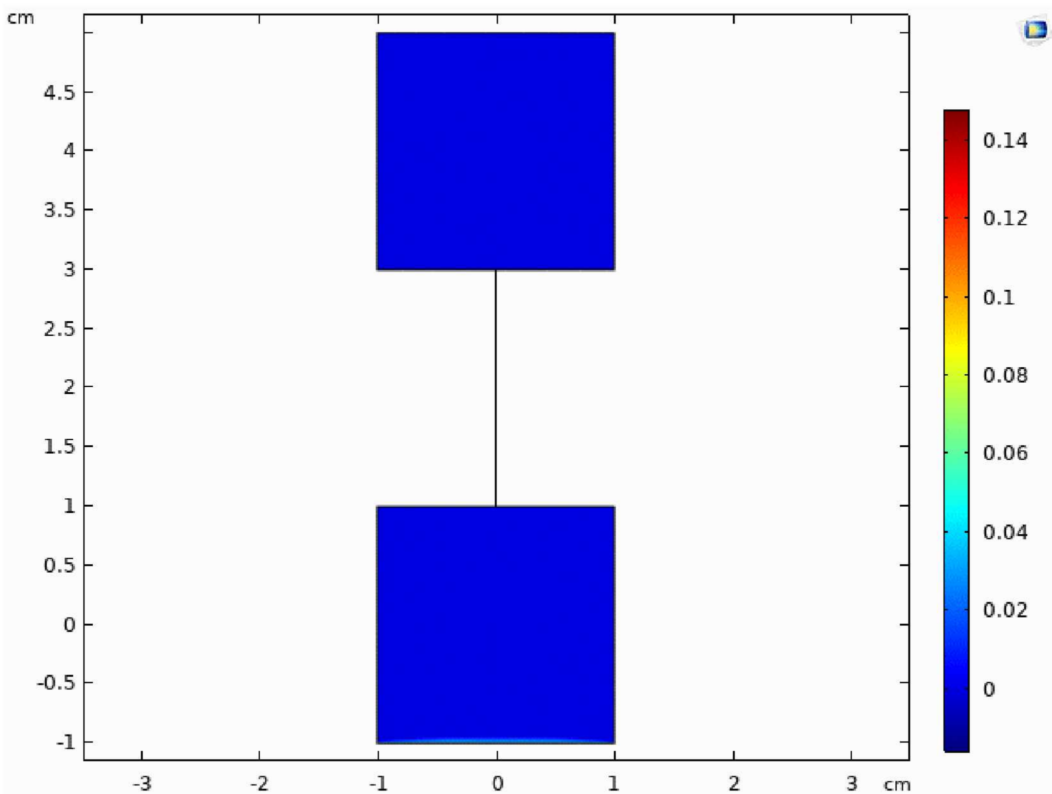


Model system from:

M.M.C. Ferreira, W.C. Ferreira Jr., A.C.S. Lino, and M.E.G. Porto, *J. Chem. Education*, vol. 76, p. 861, 1999;

H.S. Fogler and M.N. Gurmen, http://www.engin.umich.edu/~cre/web_mod/oscil/module.htm

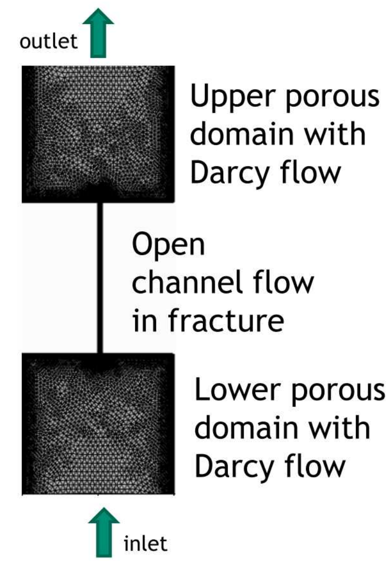
Applications: Interaction with Fractures and Leakage in Engineered Barriers

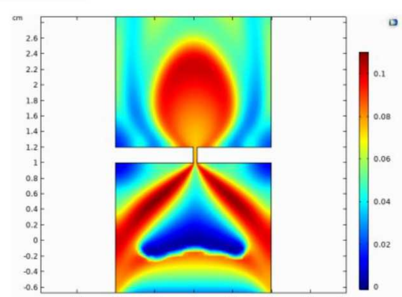


IO_3^- model; 50 micron aperture, 10^{-5} m/s

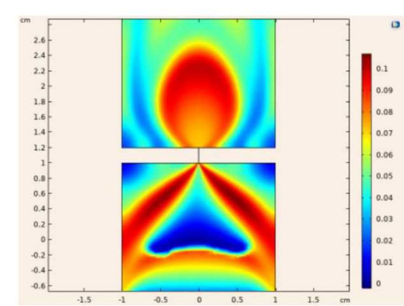
Iodate chemical waves passing through fracture-like leakage pathways show lack of sensitivity to fracture aperture

2D Forscheimer model for fracture flow



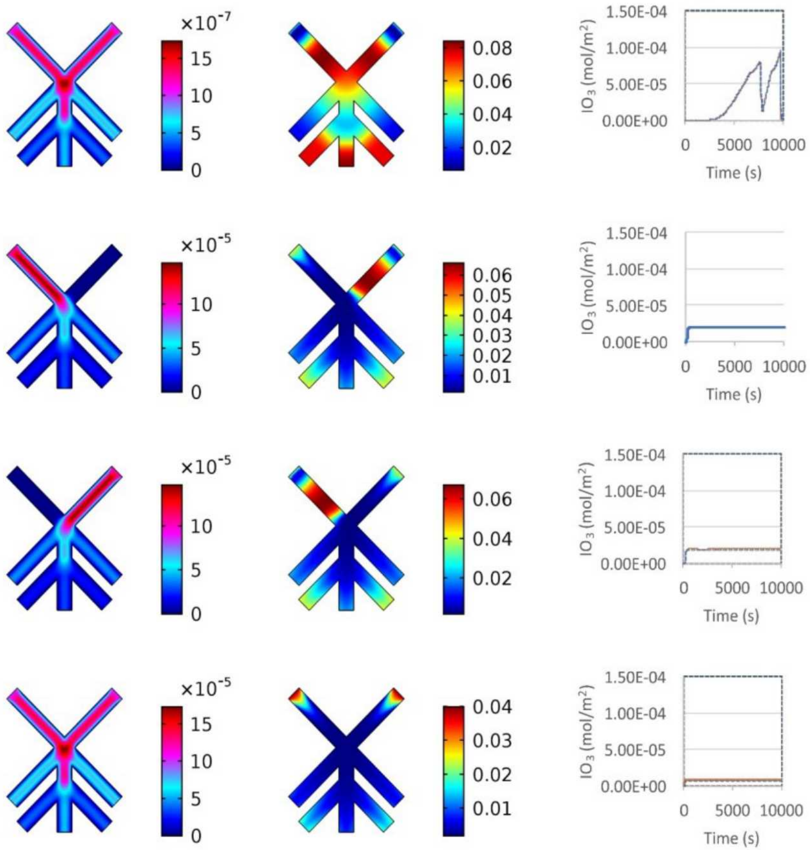


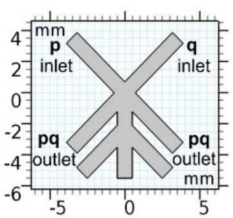
500 micron aperture, 5000 s



5 micron aperture, 5000 s

Applications: Liquid Logic Gates in Fractured Media





p	q	pq
1	1	1
1	0	0
0	1	0
0	0	0

p = 1 if: inlet has low vel.; outlow has significant oscillations
q = 1 if: inlet has low vel.; outlet has significant oscillations

CFD Models for Iodate system in simple 2D fracture network mimics Boolean functions in electronic computers

- Flow, chemical concentrations, and logic gate design for an AND logic gate.
- Left column: velocity (m/s). Middle column: iodate concentration (mol/m^3). Right column: line integral of outflow concentration for the left pq outlet (orange-solid line) and right pq outlet (blue-dashed line).
- The image and table gives the geometry and labels of inlets/outlets and the truth table.

Further Musings on Applications

A variety of autocatalytic chemical systems are known (e.g. Noyes, 1990; Orba'n et al., 2015) that could help design analogous systems that could serve as nonlinear chemical tracers in the subsurface:

- Bray-Liebhafsky reaction involving disproportioning of H_2O_2 by iodate
- Briggs-Rauscher reaction with iodate, hydrogen peroxide, and carboxylic acids
- Oscillatory dehydration of formic acid involving carbon monoxide
- Destruction of ozone by CHCs

We suggest that appropriately engineered chemical waves could serve other purposes in subsurface sensing:

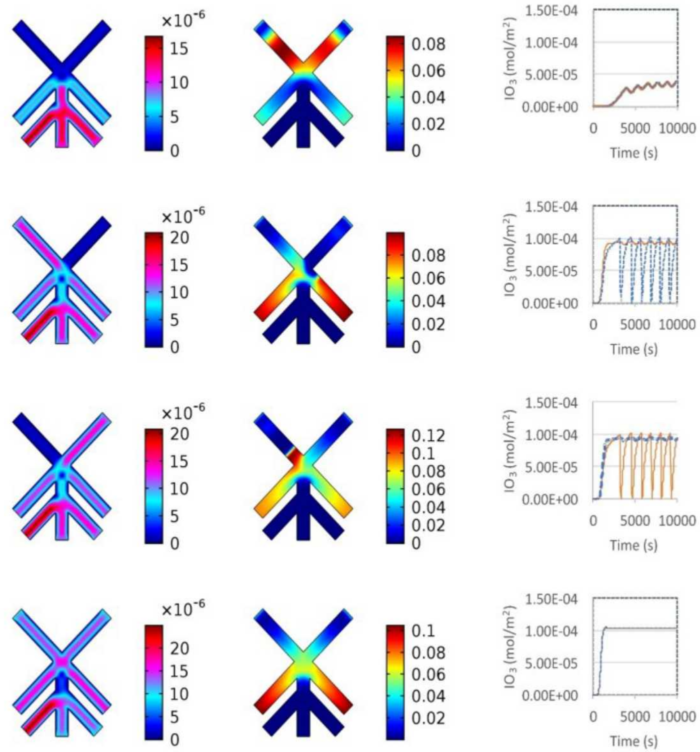
- Information or power delivery to or from embedded electronic sensors
- Swelling clays as chemo-mechanical pumps
- Interacting with microbial populations to track migrating contaminant plumes.
- Inasmuch as the kinetics of chemical waves can be fine-tuned, chemical waves can alternatively overcome temporal and spatial limitations of other subsurface sensing mechanisms, increasing resolutions below that of seismic imaging, or overcoming attenuation of electronic sensors.

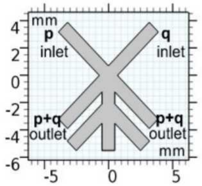
Conclusions

We suggest that simple autocatalytic reaction networks could serve as "chemical wave" or "nonlinear" tracers for subsurface sensing

A combination of microfluidic experimentation and CFD modeling of nonlinear tracing demonstrates sensitivity to flow path geometries and advective gradients, displaying excitability and a variety of wave behavior

Nonlinear tracers could prove useful for leakage and contaminant detection at sub-seismic resolutions, expanding the role of chemical tracing





p	q	p+q
1	1	1
0	1	1
1	0	1
0	0	0

p = 1 if: inlet has low vel.; outlow has significant oscillations
q = 1 if: inlet has low vel.; outlet has significant oscillations

Simple "OR" logic gates in iodate oscillator system