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Sandia National Laboratories

Novel Methods for International Safeguard Sensing: Nonlinear Chemical Waves and In Situ Logic-Tree Analysis

INMM/ESARDA Joint Annual Meeting

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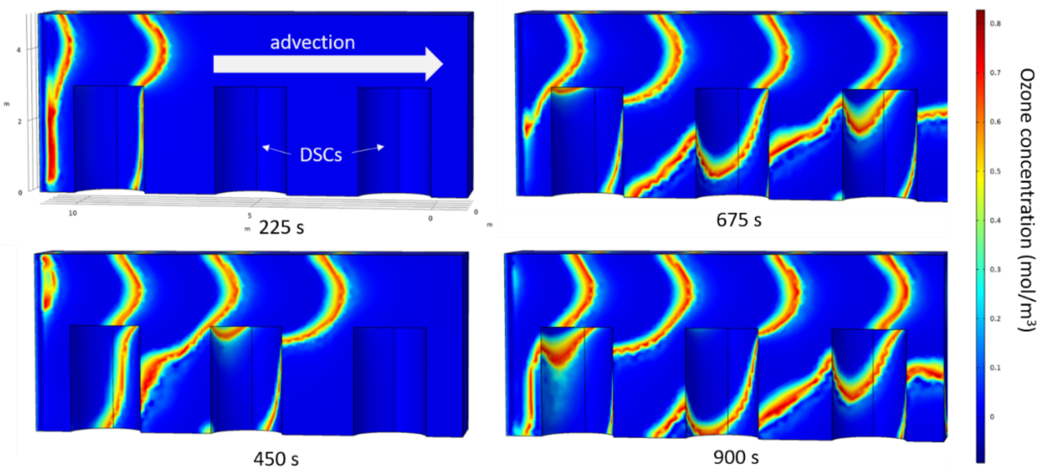

PRESENTED BY

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ENERGY NNSA

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Safeguards Sensing Using Nonlinear Chemical Waves

Goal: develop trace chemical wave sensing technologies to detect and identify

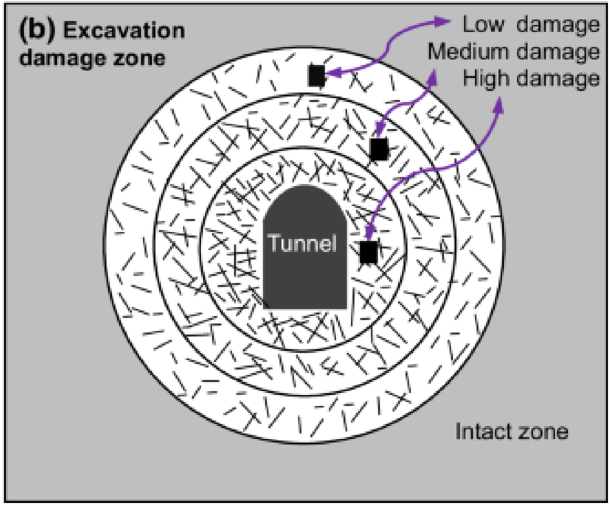
Features: chemical waves propagate information spatially and temporally to augment current methodologies for above-ground or subsurface nuclear waste storage; improving upon:

- Difficulty in verifying seals
- Problems in accessibility
- ALARA issues with exposure and dosing-out
- Large volumes/surface areas for sensing

Dry Cask Storage

Aymanns and Rezniczek, 2016

Subsurface Repositories

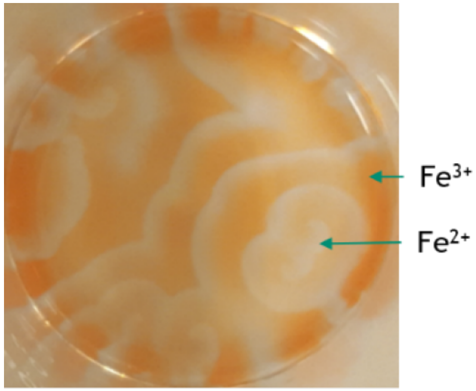


Yang et al., 2019

What are Chemical Waves??

- Chemical waves are true spatio-temporal waves stemming from nonlinear coupling of transport and chemical reaction, phase transition, or electrical excitation under far-from-equilibrium conditions; liquid or gas phase
- Transport chemical information such as pH, redox state, or concentrations
- Used in "liquid chemical computing", chemical switches, chemical neural networks, Turing machines, image processing, Boolean logic gates etc.
- Generally involve autocatalytic reaction networks (e.g. famous Belousov Zhabotinsky (BZ) reaction)
- Sensitive to environmental stimuli including geometry, advection/diffusion conditions, radiation,

BZ chemical waves



Ozone autocatalysis (after Jungwirth 2001)

$O_3 + h\nu \rightarrow 3\,{}^3O$ *(1)* *(photolytic destruction of ozone)*

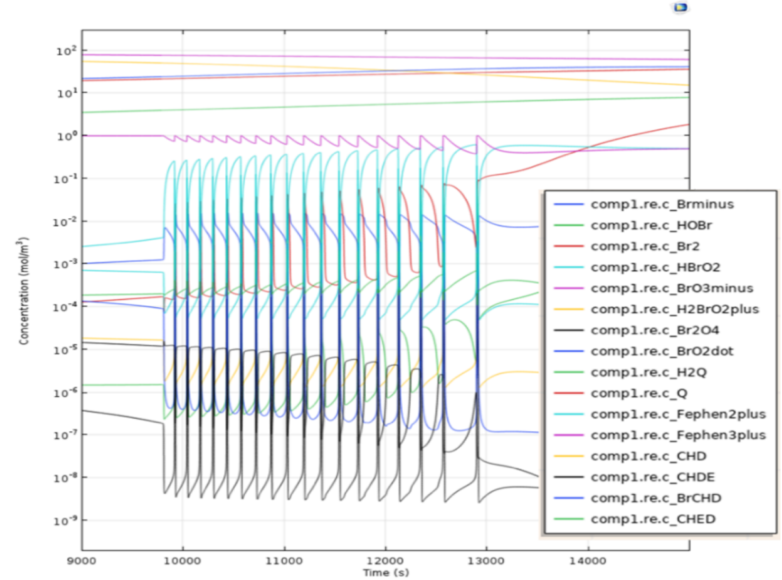
${}^3O + {}^3O_2 + M \rightarrow O_3 + M$ *(2)* *(Chapman reaction; M is N_2 or O_2)*

$3\,{}^3O + Y \rightarrow Z$ *(3)* *(Y is general species involved in exit reaction)*

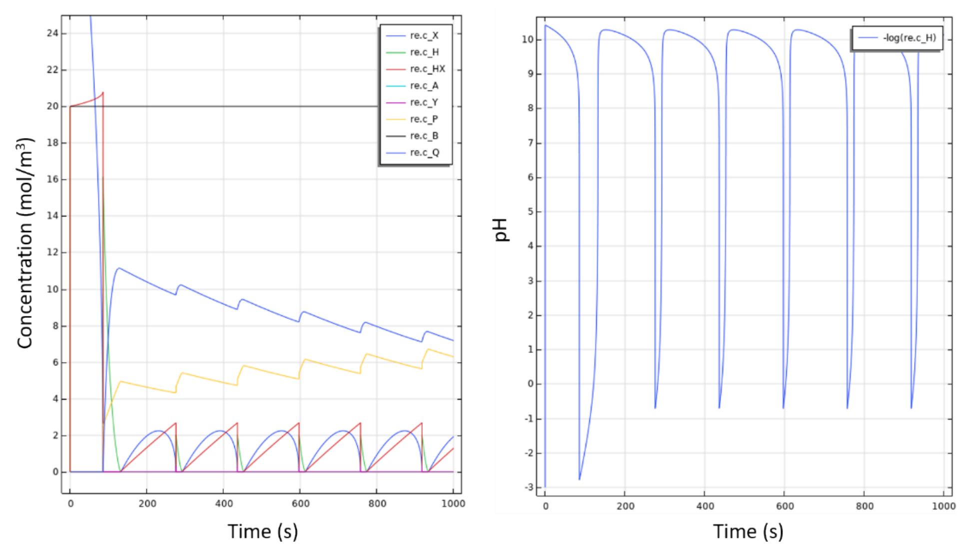
Autocatalytic Systems in Liquid Phase

- Liquid phase autocatalysis displays oscillatory behavior in different reactor schemes
- Can involve complex reaction networks, redox couples
- pH oscillators are tunable to longer frequencies
- Form the basis of spatially propagating chemical waves

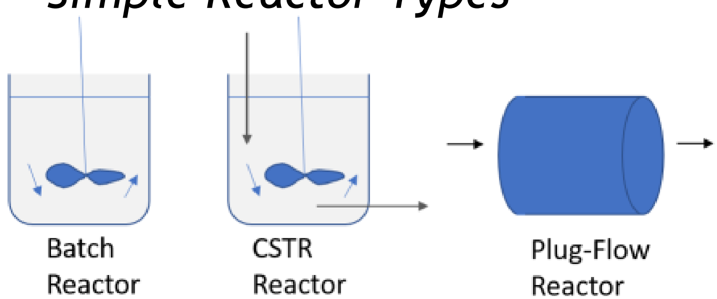
BZ Reaction in Batch Reactor



pH Oscillator in CSTR

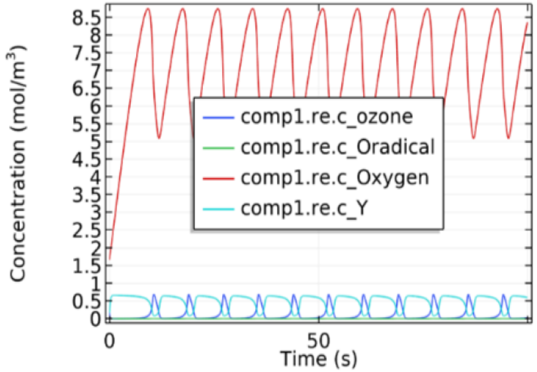


Simple Reactor Types

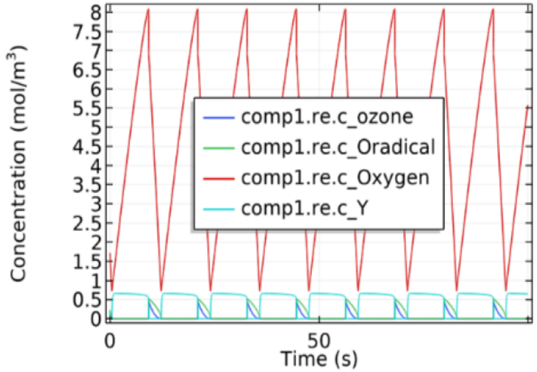


Autocatalytic Systems in Gas-Phase and Gas-Aerosol Mixtures

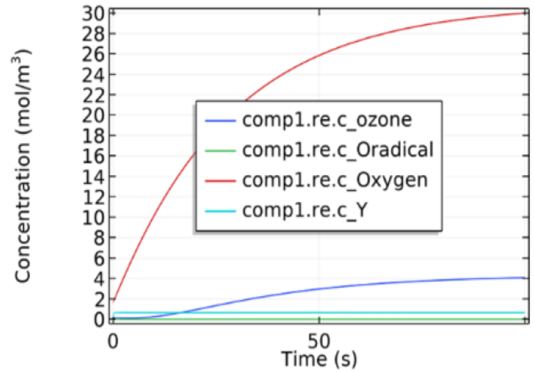
Ozone photolysis in gas phase batch reactor (COMSOL™ Model)



Rates mimic light intensity of 0.17 W/cm$_2$ (UV lamp or laser)



Rates mimic radiolytic decomposition of ozone

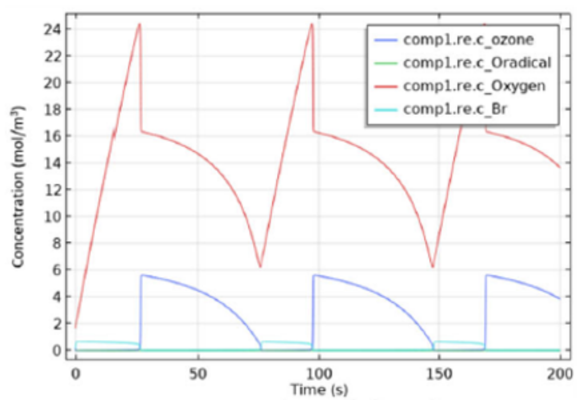


Dark Conditions

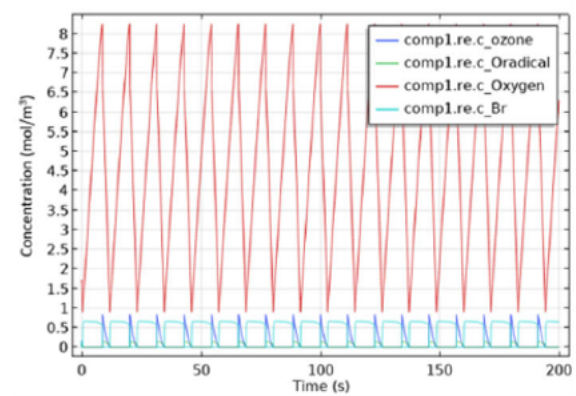
*After Jungwirth, 2001

- Radiation sources produce distinct variations in frequency and magnitude of the oscillations
- Halogen aerosols (and Nox and Vox) produce signature effects on O_3 system behavior

Ozone-halogen aerosol oscillations sensitive to different sources of ionizing radiation



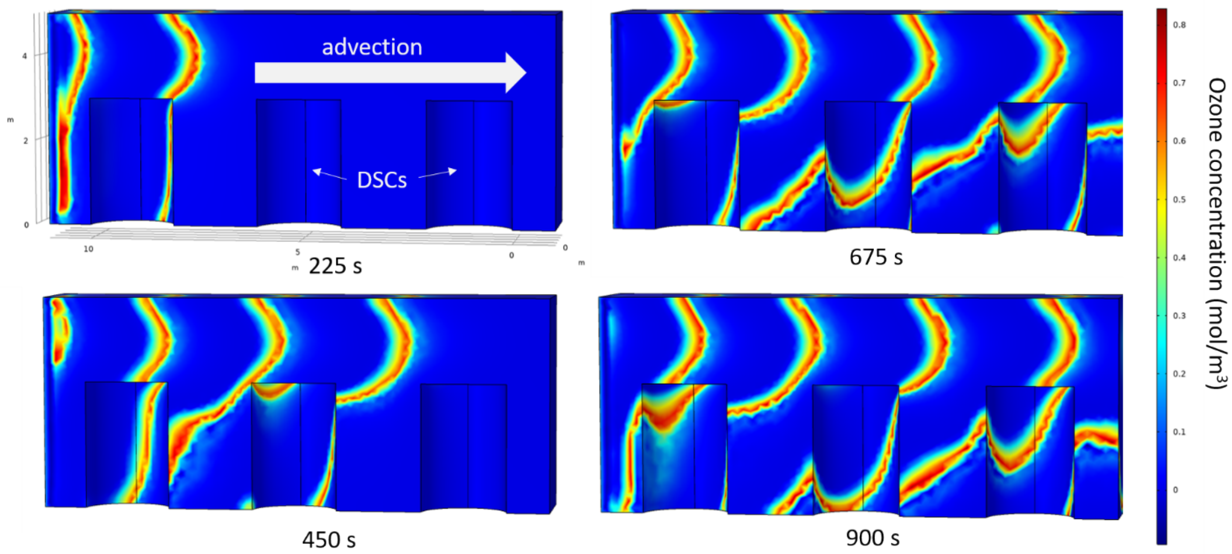
Br aerosol model with UV photocatalysis



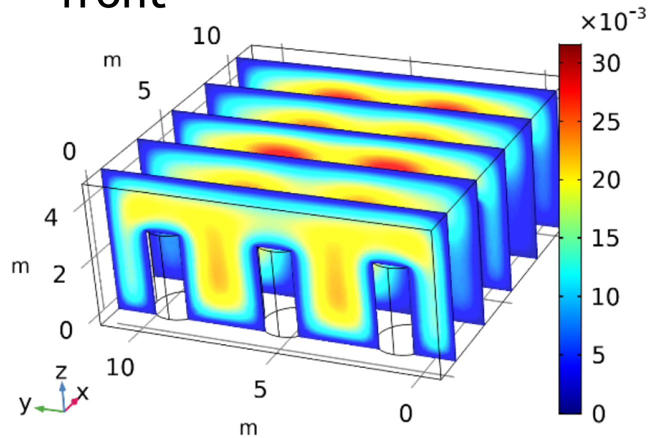
Br aerosol model with radiolysis effect on O3 dissociation

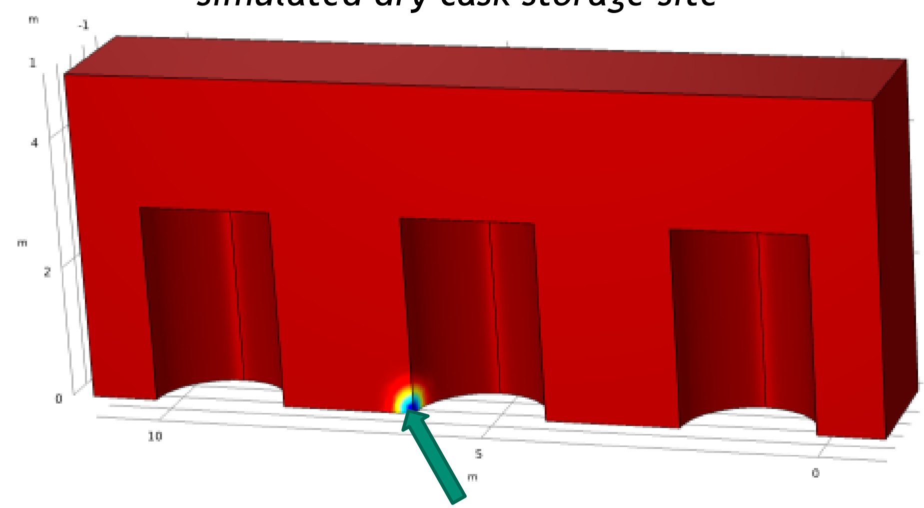
Scenario 1: Detecting Breaches in Dry Cask Storage

- Ozone system displays self organized chemical waves that fill available space
- Sensitive to wind velocity but can propagate against small advection
- A point source radiation source causes disturbance in wave front



Chemical waves of localized ozone propagate through simulated dry cask storage site





Point source from small radiation leakage is “detected” by Ozone chemical waves

Scenario 2: Application to Fractured Excavated Rock Zones (ERZs) Surrounding Subsurface Repositories

- Chemical wave dynamics are sensitive to environmental perturbations in porous fractured media, including chemical and geometric factors
- Chemical waves used for detecting new (stimulated) fracture volumes
- Phase space is a "fingerprint" of changing dynamics; inversion techniques need to be applied to detect and interpret changes

Push-Pull Modeling with Mathematica™

Field and Noyes (1974) "Oregonator" reaction network

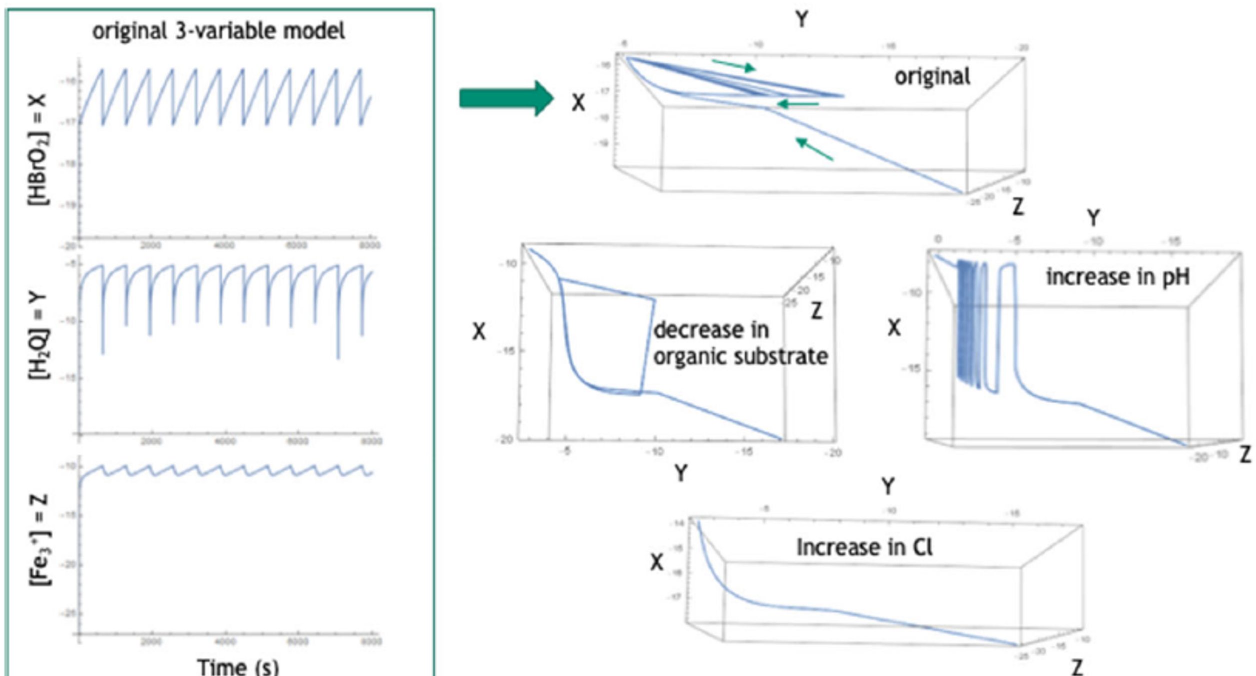
$$A + Y \rightarrow X + P$$

$$X + Y \rightarrow 2P$$

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

$$2X \rightarrow A + P$$

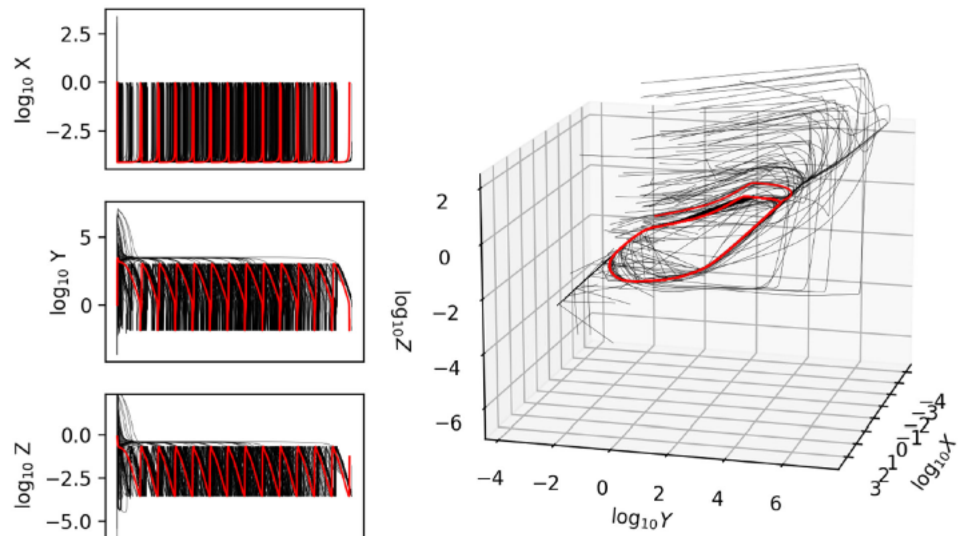
$$Z \rightarrow fY$$

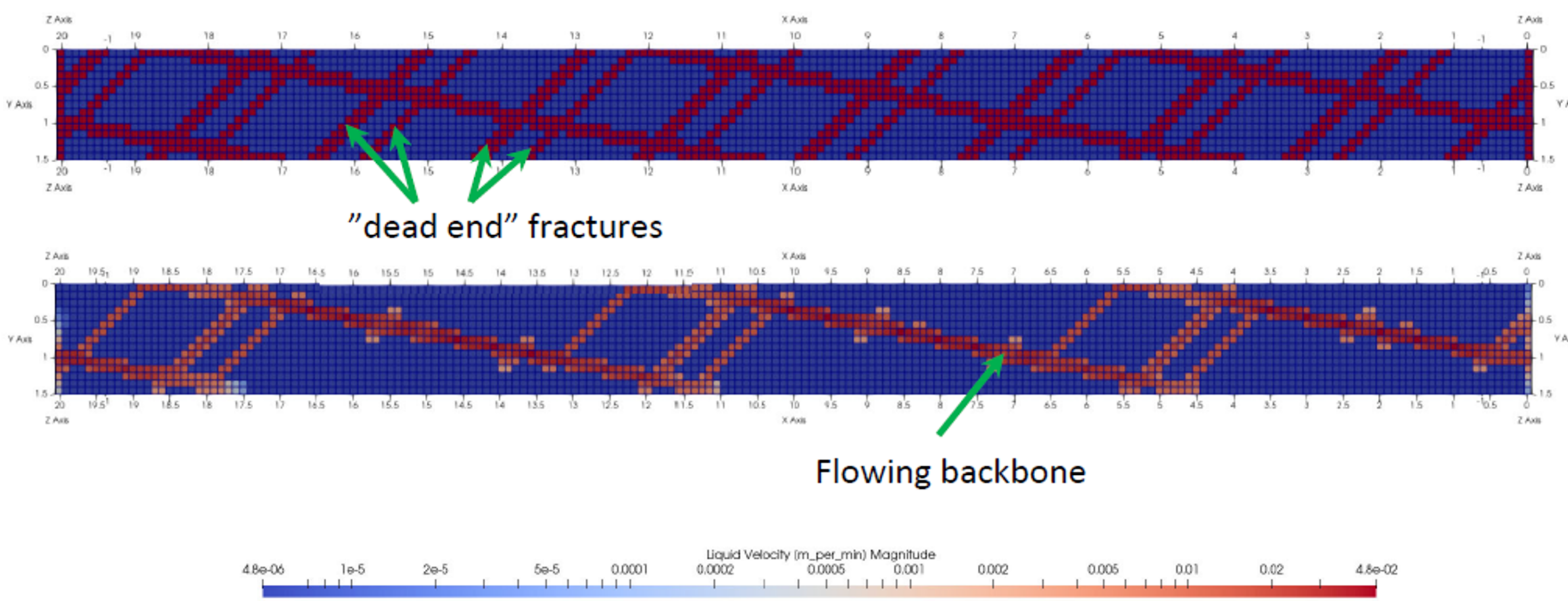


Dewers et al., 2019

Scenario 2: Chemical Wave Behavior in ERZs

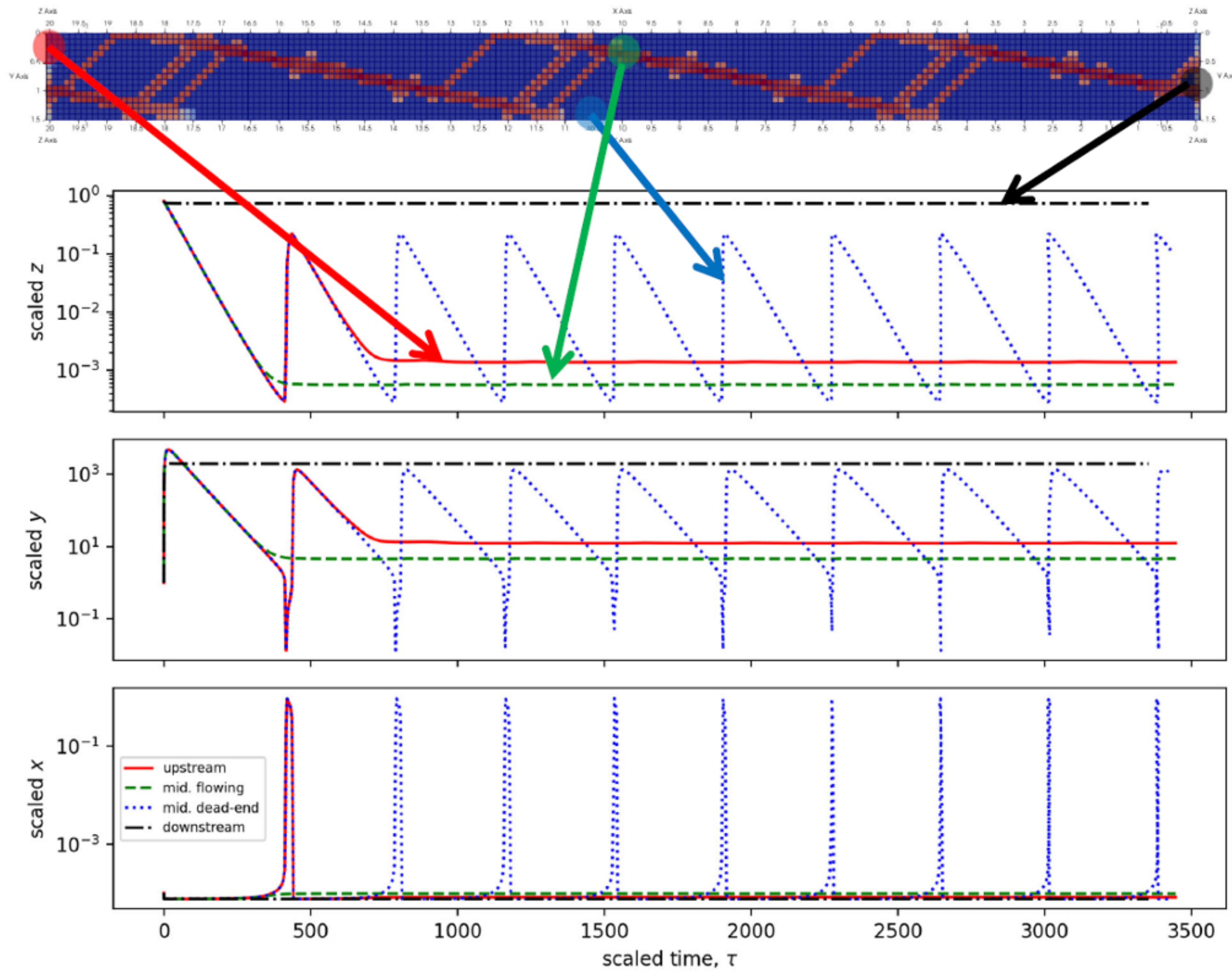
- Limit-cycle attractor is independent of initial conditions
- Sensitive to “dead volumes” and flowing backbone in fracture networks
- Modeled with PFLOTRAN





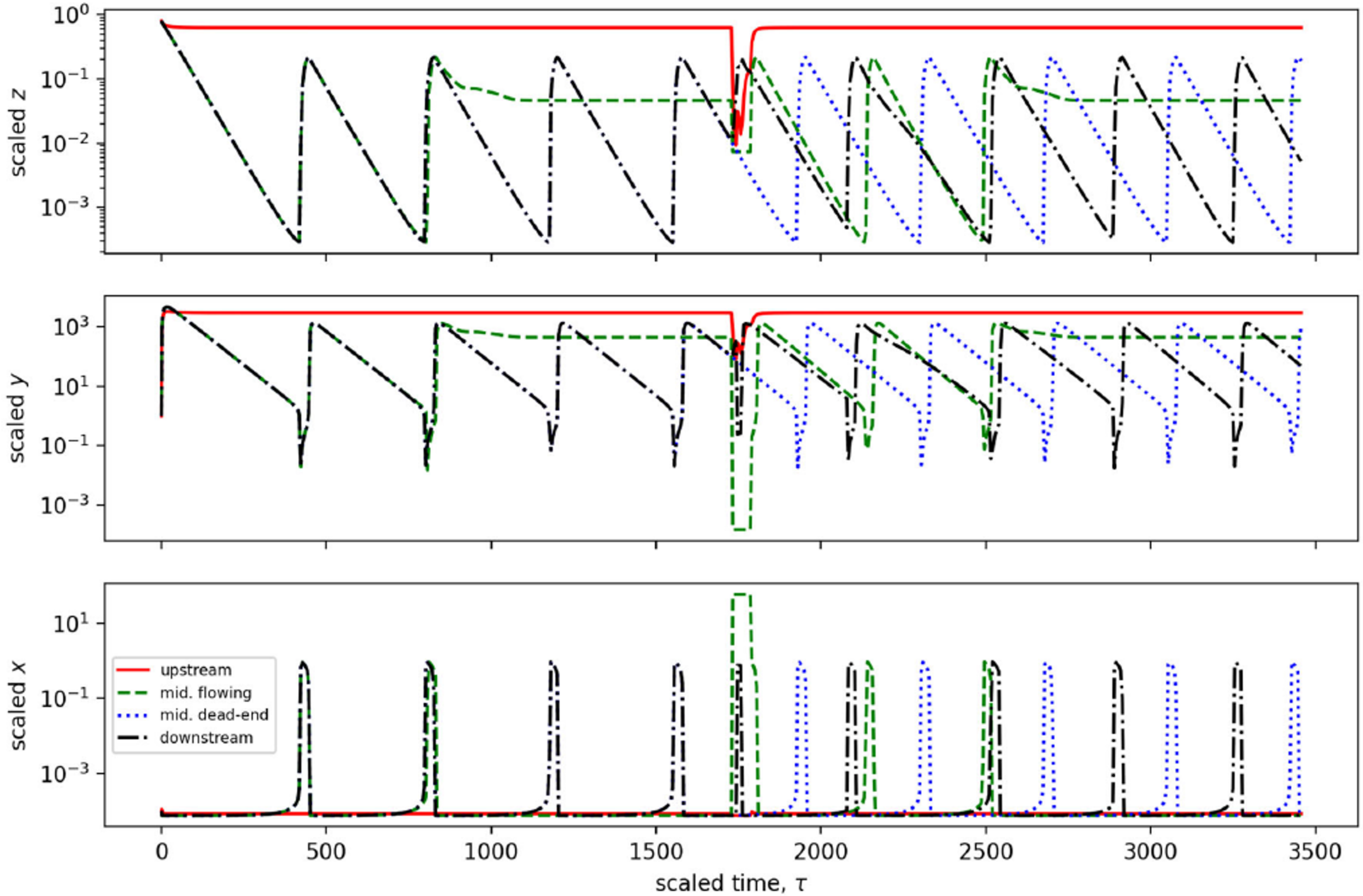
Scenario 2: Chemical Waves in Fractured Media

Higher advection can wipe out oscillations in connected volume or produce standing wave steady states. Dead volumes continue to oscillate.



Scenario 2: Detecting Intrusions in Repository ERZs

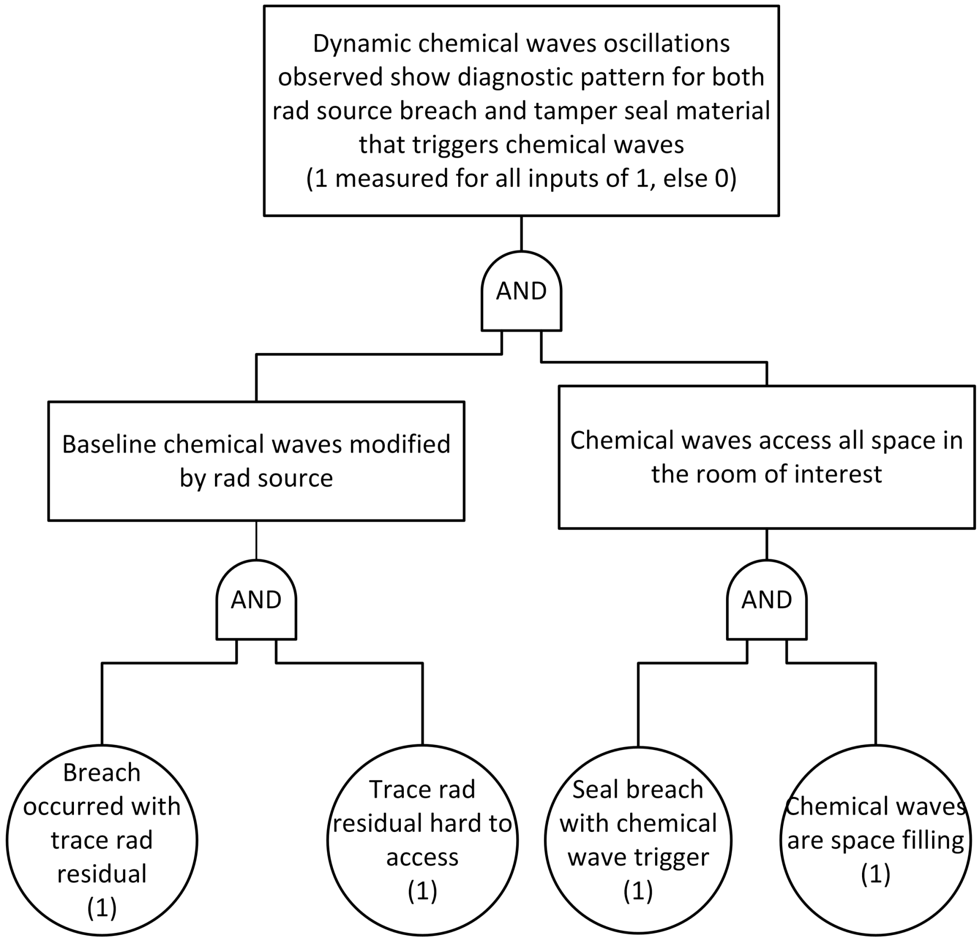
Localized perturbation in concentration perturbs the chemical wave behavior, which propagates downstream



Logic Tree Analysis of Chemical Wave Behavior

Chemical wave behavior as *in situ* logic tree analysis

- Chemical waves could answer yes/no Safeguards questions
- Organize inter-related yes/no questions into logic tree analysis
- Chemical waves themselves traverse the logic tree ***in the system itself***!
- Measurement of chemical waves answers all the questions at once



Conclusions

- We propose nonlinear chemical waves as geospatial sensors, filling space and transmitting information in Safeguards scenarios.
- Chemical waves respond to and retain a history of encountered stimuli, and the waves propagate spatially even in the absence of advection. Chemical waves can be triggered by trace quantities of solid, gaseous, or liquid chemical compounds, physico-acoustic perturbations, radiation, magnetic fields, and optical/UV stimulation.
- The trace chemical systems sense characteristics of a host medium (which could be gas or liquid phase) by producing diagnostic spatial and temporal patterns in chemical waves as triggered by what is in the host medium that is contacted by the chemicals.
- The chemical waves perform *in materio* analysis at different levels of complexity depending on the particular system and application, which may include: identification of particular substances or configurations of items in the host medium; verification that seals or other features have not been damage or removed; and/or verification that containers have not leaked a substance of interest.

Conclusions

- Chemical waves are additionally perturbed by changes in flow path topology, which presents the possibility that chemo-sensor systems could be used to detect small changes in storage containment, e.g., if a dry storage cask has been removed or otherwise altered in position or shape.
- Gas-phase or gas-aerosol oscillators could be useful for surface applications such as monitoring dry cask storage of spent fuel, or in detecting leakage in underground galleries for geologic storage of nuclear waste.
- A class of pH oscillators may be useful in subsurface applications, which could operate in fractured systems to detect containment breaches, or even changes in flow paths that could arise from engineering processes. An example of this are the universal observation of fractured or so-called disturbed zones surrounding excavated subsurface repositories in salt, shale, or granite host rocks.

Note that these systems operate at trace levels and as such do not necessarily represent an additional source of toxicity in Safeguards systems

Acknowledgments

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