

# Geofluids — Part IV

## Introduction to Geochemical and Reactive Transport Modeling

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## **Reactive transport modeling**

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# **Reactive transport modeling**

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## **Introduction**

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- **Reactive transport (RT) modeling** is an essential tool for the **analysis of coupled physical, chemical, and biological processes** in Earth systems.
- **Reactive transport models** have been applied to understand bio-geochemical systems for more than **three decades**.
- Modeling of interactions of processes at a range of spatial and time scales → connecting these process (material capabilities) at the atomic and the macroscopic scales.
- **Reactive transport models** predicts the distribution in space and time of the chemical reactions that occur along a flow-path.
- It is **essential for interpreting** the phenomena occurring in the surface or subsurface systems, as well as engineering and environmental problems:
  - reactive fluid flow (in tanks, reactors, or membranes),
  - solute transport (e.g., particles and species in the atmosphere),
  - geochemical reactions (e.g., gas and oil industry, migrating magma), and
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# Applications

- Description of **elemental and nutrient fluxes between major Earth reservoirs:**
  - understanding the natural waters composition;
  - precipitation / dissolution of rocks (minerals) in geologic formations after injection of industrial wastes / steam / CO<sub>2</sub>;
  - generation of acidic waters and leaching of metals from mine wastes.
- Treatment of **contaminant retardation in the subsurface:**
  - migration of contaminant plumes;
  - the mobility of radionuclides in waste repositories;
  - the bio-degradation of chemicals in landfills.
- Treatment of **deep Earth processes such as metamorphism and magma transport.**



(a) Acid mine drainage



(b) Yellow slime mold



(c) A landfill in Poland

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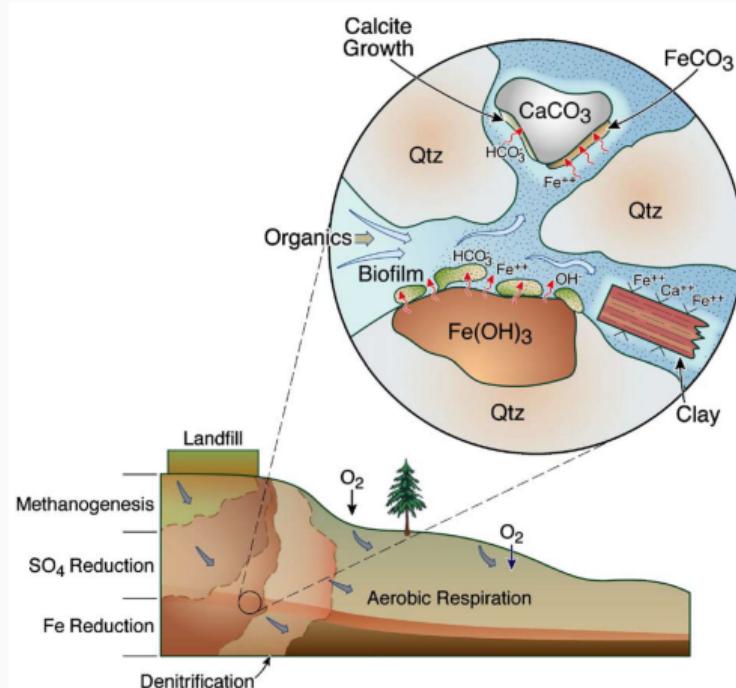


(h) Yellow slime mold



(i) A landfill in Poland

# Example of coupled processes



**Figure 1:** Illustration from Steefel et al. (2005): **coupled geochemical, microbiological, and hydrologic processes operating at both the aquifer and pore scale**, i.e., oxidation-reduction zones developed in an aquifer downstream from an organic-rich landfill.

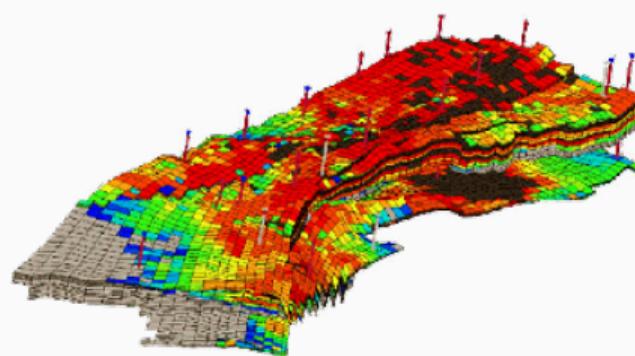
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**Petroleum reservoir simulation**

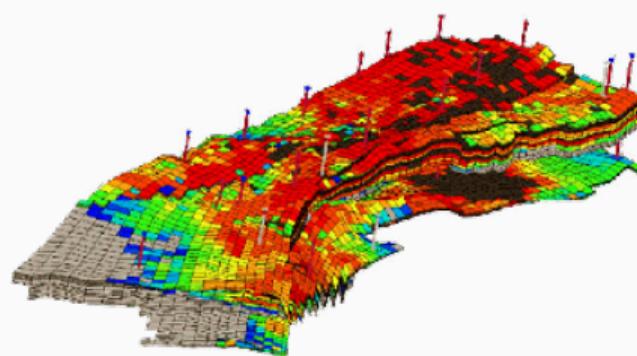
# Petroleum reservoir simulation

- **Important characteristics** of reservoir are the nature of the **rock and the fluids filling it**.
- **Reservoir characteristics**:
  - heterogeneous;
  - properties heavily depend on the space location.
- Example: **fractured reservoir** is a set of heterogeneous porous media blocks (the matrix) and a net of fractures. **Rock properties** (permeability) in such a reservoir dramatically change:
  - permeability in the matrix is 1 millidarcy;
  - permeability in the fractures is 1000 millidarcy.



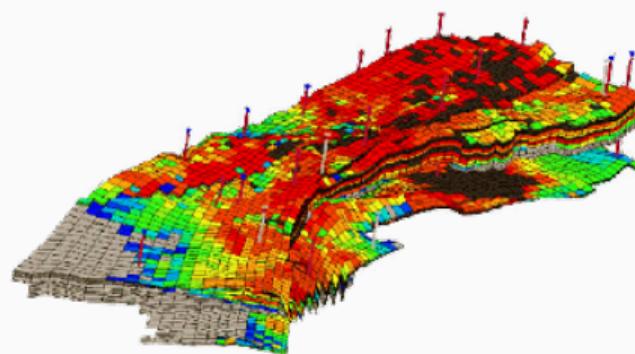
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# Stages of oil recovery

The nature of the fluids filling in reservoir strongly depends on the **stage of oil recovery**:

- **Early stage / primary recovery:**

- single fluid (gas/oil),
- high pressure,
- gas/oil is produced by natural decompression without pumping effort at the wells,
- stage ends when a pressure equilibrium between the oil field and the atmosphere occurs.

- **Secondary recovery stage** (to recover part of the remaining oil):

- fluid is injected through injection wells,
- oil is produced through production wells,
- high reservoir pressure,
- high flow rates,
- $\begin{cases} P_{\text{reservoir}} \geq P_{\text{bubble}} : \text{ two-phase immiscible flow (water and oil phases),} \\ P_{\text{reservoir}} < P_{\text{bubble}} : \text{ the flow is of the oil type.} \end{cases}$

# Enhanced oil recovery techniques

- **Water flooding**
  - is not very effective: > 50% of hydrocarbons often remain in the reservoir;
  - large amount of oil is trapped in small pores and cannot be washed out;
  - the oil is heavy and viscous, whereas the water is extremely mobile ⇒ with sufficiently high flow rates, the production wells primarily produce water instead of oil.
- **Enhanced recovery techniques** (using complex chemical and thermal effects) is injecting materials that are not normally present in a petroleum reservoir.
- **Main objective** of these techniques is to achieve **miscibility** (and thus **eliminate the residual oil saturation oil**) by
  - increasing temperature (e.g., in situ combustion) or
  - injecting other chemical species (e.g., CO<sub>2</sub>).
- Popular enhanced recovery techniques:
  - **composition flow** (given chemical composition, the rest is dependent on the thermodynamic conditions and the overall concentration of each species);
  - **thermal methods** (steam drive and soak);
  - **chemical flooding** (alkaline, surfactant, polymer, and foam flooding).

## **Reactive transport modeling**

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**Advection-diffusion-reaction equation**

## Advection-diffusion-reaction equation (transport equation) i

- Conservation laws permit us to derive the following partial differential equation that governs the **transport of a conservative quantity**  $u$ :

$$\frac{\partial u}{\partial t} + \nabla \cdot (\mathbf{v}u - D\nabla u) + \rho(u) = f \quad \mathbf{x} \in \Omega, t > 0$$

- **Quiz:** which operator in this equation could be responsible for the reactive part of the modeling?

<http://etc.ch/JTfB/?qr> or



## Advection-diffusion-reaction equation (transport equation) ii

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where

- $\frac{\partial u}{\partial t}$  is the **time derivative**;
- $\nabla u = \begin{pmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} & \frac{\partial u}{\partial z} \end{pmatrix}$  is the **gradient operator** of scalar variable  $u$  denoting **flux** and in combination with  $D$  accounting for the **diffusion/dispersion processes**;
- $\nabla \cdot \mathbf{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$  is the **divergence operator** of vector variable  $\mathbf{v}$  accounting **convection/advection**;
- $\rho(u)$  is the **reaction operator**.

## Advection-diffusion-reaction initial boundary value problem (I-BVP)

- Adding initial and boundary condition, we obtain **initial boundary value problem (I-BVP)**

$$\partial u / \partial t + \nabla \cdot (\mathbf{v} u - D \nabla u) + \rho(u) = f \quad \mathbf{x} \in \Omega, t > 0$$

$$u = u_0 \quad \mathbf{x} \in \Omega, t = 0$$

$$u = u_D \quad \mathbf{x} \in \Gamma_D, t > 0$$

$$\mathbf{v} u - D \nabla u = g \quad \mathbf{x} \in \Gamma_N, t > 0$$

- $u$  is some **conservative quantity** (e.g., energy, species amounts) per volume;
- $\mathbf{v}$  is the **velocity field** in which the quantity is advected;
- $D$  is a **dispersion–diffusion tensor**;
- $f$  is a **rate of generation** (e.g., heat generation, reaction rate).
- $u_0$  is the **given initial condition** of  $u$  at time  $t = 0$  at every  $x$  in the domain  $\Omega$ ;
- $u_D$  is the **given value** of  $u$  on a **Dirichlet boundary**  $\Gamma_D$ ;
- $g$  is the **given value** of the flux  $\mathbf{v} u - D \nabla u$  on a **Neumann boundary**  $\Gamma_N$ .

## Exercise, 1D advection-diffusion equation

- **Exercise:** Write the partial differential equation

$$\frac{\partial u}{\partial t} + \nabla \cdot (\mathbf{v}u - D\nabla u) + \rho(u) = f$$

for the **one dimensional case** with  $u = u(t, x)$  and a scalar velocity  $v$ .

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- **Answer:** one dimensional case of the equation above reads as follows:

$$\frac{\partial u}{\partial t} + \frac{\partial}{\partial x} \left( vu - D \frac{\partial u}{\partial x} \right) + \rho(u) = f.$$

Alternatively, we can apply the operator  $\partial/\partial x$  on each term inside parenthesis to get

$$\frac{\partial u}{\partial t} + \frac{\partial(vu)}{\partial x} - \frac{\partial}{\partial x} \left( D \frac{\partial u}{\partial x} \right) + \rho(u) = f.$$

## Exercise, 1D advection-diffusion equation (constant diffusion and velocity)

- **Exercise:** Assume velocity  $v$  and diffusion coefficient  $D$  are constant. How can we simplify

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- **Answer:** We move both  $v$  and  $D$  outside the derivative

$$\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial x} - D \frac{\partial^2 u}{\partial x^2} + \rho(u) = f.$$

## First-order splitting to transport and reaction equations

- Let us represent

$$\frac{\partial u}{\partial t} + \nabla \cdot (\mathbf{v}u - D\nabla u) + \rho(u) = 0 \quad \text{as} \quad \frac{\partial u}{\partial t} + T(u) + R(u) = 0$$

where  $T(u)$  and  $R(u)$  are transport and reaction operators.

- According to the first-order splitting, we first solve the transport equation for  $\bar{u}$ , i.e.,

$$\begin{aligned}\frac{\partial \bar{u}}{\partial t} + T(\bar{u}) &= 0, & t > 0, \\ \bar{u} &= u_0, & t = 0,\end{aligned}$$

and next the reaction equation with reconstructed  $\bar{u}$  as the initial condition, i.e.,

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## Reaction equation in terms of chemical kinetic-equilibrium problem

- Reaction equation

$$\begin{aligned}\frac{\partial u}{\partial t} + R(u) &= 0, \quad t > 0, \\ u &= \bar{u}, \quad t = 0,\end{aligned}$$

is already discussed **chemical kinetic-equilibrium differential-algebraic equation (DAE)**

$$\begin{aligned}\frac{db_e}{dt} &= f_e(n_e), \quad t > 0, \\ \frac{dn_k}{dt} &= f_k(n_k), \quad t > 0, \\ n_e &= \varphi(T, P, b_e), \quad t > 0, \\ b_e &= An_e^o, \quad t = 0, \\ n_k &= n_k^o, \quad t = 0.\end{aligned}$$

# Numerical solution of the transport equations

- There are many **numerical methods for the solution of the I-BVP** with transport equation

$$\frac{\partial u}{\partial t} + T(u) = f.$$

- **Finite difference method (FDM):**

- is the **simplest** of all methods,
- has **disadvantages** when **complex geometries** are involved.

- **Finite volume method (FVM):**

- forces **conservation of quantities** at discretized level,
- only needs to do flux evaluation for the cell boundaries,
- can be used on **unstructured (triangular) grids**,
- the higher-order approximations are not easily constructed.

- **Finite element method (FEM):**

- applicable to **general boundary conditions**, **complex geometry**, and **variable material properties**,
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## Basics of finite difference method (FDM)

- In the **FDM**, the derivatives are approximated with **finite difference formulas**.
- The **Taylor expansion** is a **polynomial** approximation of function  $f$  around a point  $x_i$

$$f(x_i + \Delta x) = f(x_i) + \frac{\partial f(x_i)}{\partial x} \Delta x + \frac{1}{2} \frac{\partial^2 f(x_i)}{\partial x^2} \Delta x^2 + \cdots + \frac{1}{n!} \frac{\partial^n f(x_i)}{\partial x^n} \Delta x^n + \cdots$$

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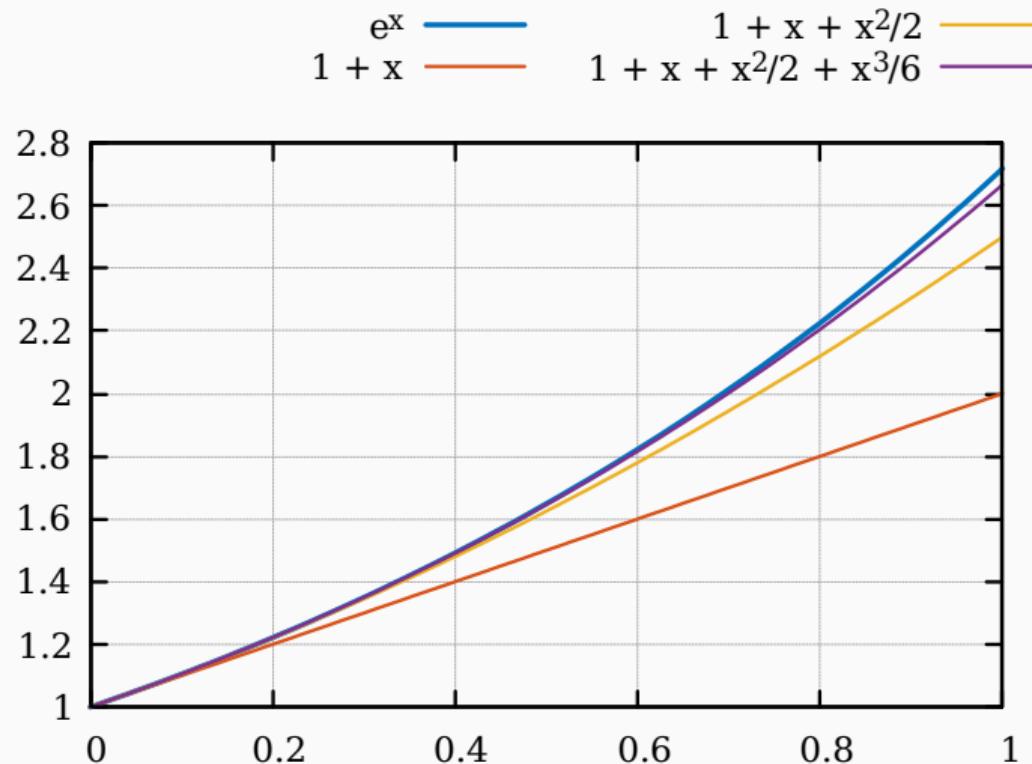
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- **Exercise:** Write the Taylor expansion for  $f(x) = e^x$  around  $x_i = 0$ .
- **Answer:**

$$f(x_i + h) = e^{x_i + \Delta x} \approx 1 + \Delta x + \frac{1}{2} \Delta x^2 + \frac{1}{6} \Delta x^3 + \cdots$$

## Approximation of $e^x$ using Taylor series



## First-order FDM scheme

- We can derive **finite difference approximations** for derivatives  $\frac{\partial f(x_i)}{\partial x}$ ,  $\frac{\partial^2 f(x_i)}{\partial x^2}$ , etc by truncating the Taylor expansion

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up until the **derivative order**.

- For example, for **1st order approximation**

$$f(x_i + \Delta x) \approx f(x_i) + \frac{\partial f(x_i)}{\partial x} \Delta x + O(\Delta x^2) \implies \frac{\partial f(x_i)}{\partial x} \approx \frac{f(x_i + h) - f(x_i)}{\Delta x} + O(\Delta x),$$

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up until the **derivative order**.

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$$f(x_i + \Delta x) \approx f(x_i) + \frac{\partial f(x_i)}{\partial x} \Delta x + O(\Delta x^2) \implies \frac{\partial f(x_i)}{\partial x} \approx \frac{f(x_i + h) - f(x_i)}{\Delta x} + O(\Delta x),$$

the error decrease is of order  $O(h)$  with decreasing  $h$ .

- **Exercise:** Derive the **second order approximation**, where the approximation error is proportional to  $O(h^2)$  with a decrease of  $h$ ?

## Second-order FDM scheme, Central difference approximation

- Write the following two **truncated Taylor expansions**:

$$f(x_i + \Delta x) = f(x_i) + \frac{\partial f(x_i)}{\partial x} \Delta x + \frac{1}{2} \frac{\partial^2 f(x_i)}{\partial x^2} \Delta x^2 + O(\Delta x^3)$$

$$f(x_i - \Delta x) = f(x_i) - \frac{\partial f(x_i)}{\partial x} \Delta x + \frac{1}{2} \frac{\partial^2 f(x_i)}{\partial x^2} \Delta x^2 + O(\Delta x^3)$$

- By subtracting the two equations, we can write

$$\frac{\partial f(x_i)}{\partial x} \approx \frac{f(x_i + \Delta x) - f(x_i - \Delta x)}{2\Delta x} + O(\Delta x^2)$$

which is a **central finite difference approximation** for  $\partial f(x_i)/\partial x$ .

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## Usage of FDM to transform differential equation

- We use the **finite difference formulas**

$$\frac{\partial f(x_i)}{\partial x} \approx \frac{f(x_i + \Delta x) - f(x_i - \Delta x)}{2\Delta x}$$

and

$$\frac{\partial^2 f(x_i)}{\partial x^2} \approx \frac{f(x_i + \Delta x) - 2f(x_i) + f(x_i - \Delta x)}{\Delta x^2}$$

to transform the **partial differential equation** (PDE)

$$\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial x} - D \frac{\partial^2 u}{\partial x^2} = f \quad \text{on} \quad [x_L, x_R]$$

into a **system of linear algebraic equations**.

## Discretization of transport equation, Computational domain discretization

- We numerically solve the transport problem

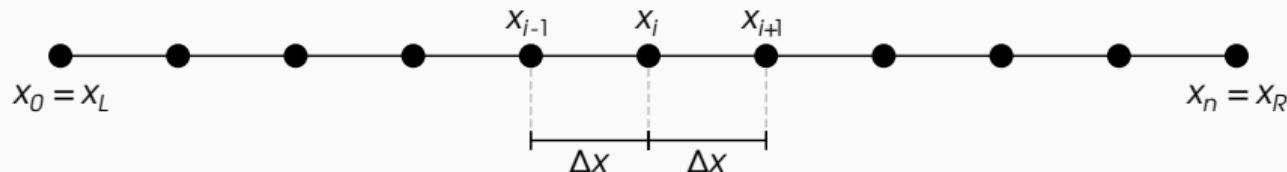
$$\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial x} - D \frac{\partial^2 u}{\partial x^2} = f \quad x_L < x < x_R, \quad t > 0,$$

$$u = 0 \quad x_L < x < x_R, \quad t = 0,$$

$$u = 1 \quad x = x_L, \quad t > 0,$$

and free boundary at  $x = x_R$  using the finite difference method (FDM).

- Consider the following uniform discretization of computational domain  $[x_L, x_R]$ :



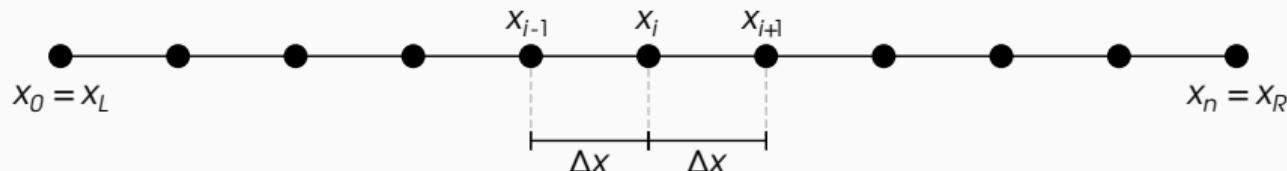
## Discretization of transport equation, Finite difference formulas

- Using **finite difference formulas**, we can approximate the partial derivatives in transport equation as follows:

$$\frac{\partial u}{\partial t} \approx \frac{u_i^{k+1} - u_i^k}{\Delta t} \quad x = x_i, t = t_k$$

$$\frac{\partial u}{\partial x} \approx \frac{u_{i+1}^{k+1} - u_{i-1}^{k+1}}{2\Delta x} \quad x = x_i, t = t_k$$

$$\frac{\partial^2 u}{\partial x^2} \approx \frac{u_{i+1}^{k+1} - 2u_i^{k+1} + u_{i-1}^{k+1}}{\Delta x^2} \quad x = x_i, t = t_k$$



## Discretization of transport equation: system of algebraic equations

- The differential equation

$$\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial x} - D \frac{\partial^2 u}{\partial x^2} = f$$

becomes a **system of algebraic equations**

$$\left( \frac{u_i^{k+1} - u_i^k}{\Delta t} \right) + v \left( \frac{u_{i+1}^{k+1} - u_{i-1}^{k+1}}{2\Delta x} \right) - D \left( \frac{u_{i+1}^{k+1} - 2u_i^{k+1} + u_{i-1}^{k+1}}{\Delta x^2} \right) = f_i \quad (i = 1, \dots, n-1)$$

- With **recovered values**  $u_i^k$  ( $u$  on every **discrete point**  $x_i$  at **discrete time**  $t_k$ ), we solve algebraic equations to find  $u_i^{k+1}$  ( $u$  on every  $x_i$  at  $t_{k+1} = t_k + \Delta t$ ):

$$u_i^{k+1} + \frac{v \Delta t}{2\Delta x} \left( u_{i+1}^{k+1} - u_{i-1}^{k+1} \right) - \frac{D \Delta t}{\Delta x^2} \left( u_{i+1}^{k+1} - 2u_i^{k+1} + u_{i-1}^{k+1} \right) = \Delta t f_i + u_i^k \quad (i = 1, \dots, n-1)$$

## Discretization of transport equation: central vs. upwind scheme

- The **central scheme** for the finite difference approximation of the advection term, i.e.,

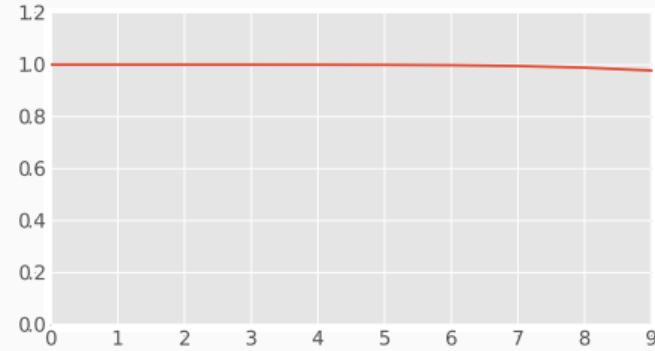
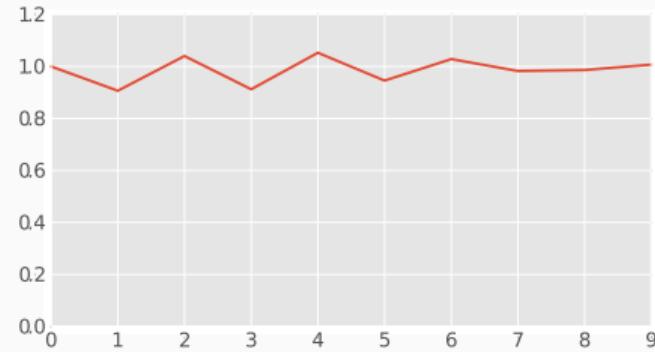
$$v \frac{\partial u}{\partial x} \approx v \left( \frac{u_{i+1}^{k+1} - u_{i-1}^{k+1}}{2\Delta x} \right),$$

can produce **spurious oscillations**.

- One can use instead an **upwind scheme**, i.e.,

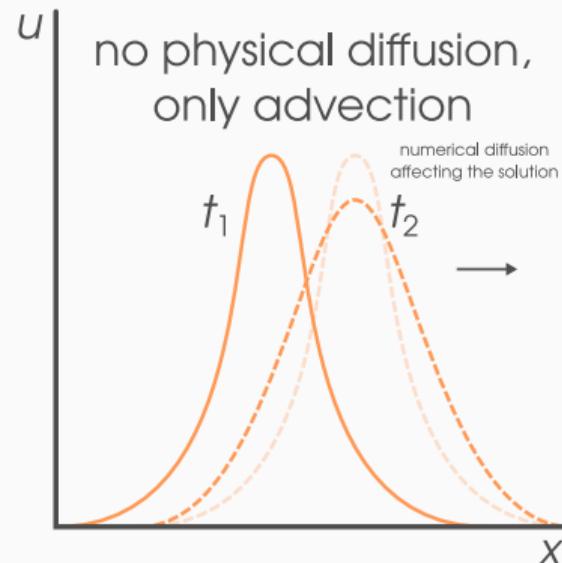
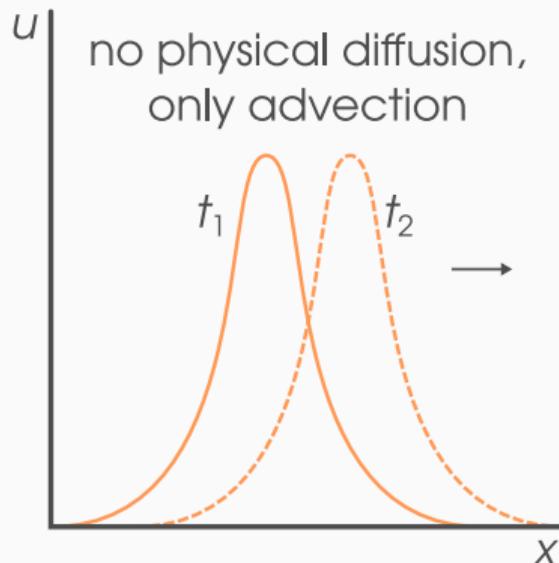
$$v \frac{\partial u}{\partial x} \approx v \left( \frac{u_i^{k+1} - u_{i-1}^{k+1}}{\Delta x} \right),$$

to prevent this.



# Numerical diffusion introduced by the upwind scheme

- **Warning:** the upwind scheme fixes the numerical oscillation, but introduces **numerical diffusion!**



## Discretization of transport equation: tridiagonal formulation

- We write the algebraic equation

$$\left( \frac{u_i^{k+1} - u_i^k}{\Delta t} \right) + v \left( \frac{u_i^{k+1} - u_{i-1}^{k+1}}{\Delta x} \right) - D \left( \frac{u_{i+1}^{k+1} - 2u_i^{k+1} + u_{i-1}^{k+1}}{\Delta x^2} \right) = f_i \quad (i = 1, \dots, n-1)$$

into the the following tridiagonal matrix form:

$$a_i u_{i-1}^{k+1} + b_i u_i^{k+1} + c_i u_{i+1}^{k+1} = d_i \quad (i = 1, \dots, n-1)$$

- **Tridiagonal matrix** is a band matrix that has nonzero elements on the main diagonal and first diagonal below and above it the main one.
- **Exercise:** Find the values of the coefficients  $a_i, b_i, c_i$ , and  $d_i$ .

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## Discretization of transport equation: internal points

- For **every internal point**  $x_i$ , we have the system

$$a_i u_{i-1}^{k+1} + b_i u_i^{k+1} + c_i u_{i+1}^{k+1} = d_i \quad (i = 1, \dots, n-1)$$

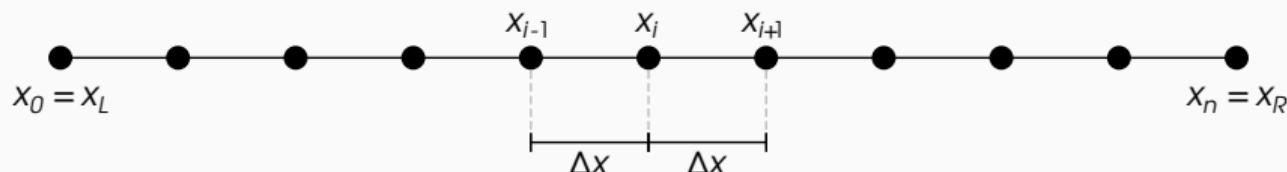
where

$$a_i = -\frac{v\Delta t}{\Delta x} - \frac{D\Delta t}{\Delta x^2}$$

$$b_i = 1 + \frac{v\Delta t}{\Delta x} + 2\frac{D\Delta t}{\Delta x^2}$$

$$c_i = -\frac{D\Delta t}{\Delta x^2}$$

$$d_i = u_i^k + \Delta t f_i$$



## Discretization of transport equation: left boundary condition

- On the **left boundary point**,  $u = 1$ , and thus  $u_0^k = u_0^{k+1} = 1$ .
- **Exercises:** What are the values of  $a_0$ ,  $b_0$ ,  $c_0$  and  $d_0$  in the general equation:

$$a_0 u_{-1}^{k+1} + b_0 u_0^{k+1} + c_i u_1^{k+1} = d_0?$$

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$$a_0 u_{-1}^{k+1} + b_0 u_0^{k+1} + c_i u_1^{k+1} = d_0?$$

- **Answer:**

$$a_0 = 0$$

$$b_0 = 1$$

$$c_0 = 0$$

$$d_0 = 1$$

## Discretization of transport equation: right boundary condition

- On the **right boundary point**, we use the following finite difference representation for the **advection** and **diffusion terms**:

$$\left( v \frac{\partial u}{\partial x} \right)_n^{k+1} = v \frac{u_n^{k+1} - u_{n-1}^{k+1}}{\Delta x} \quad \text{and} \quad \left( D \frac{\partial^2 u}{\partial x^2} \right)_n^{k+1} = 0.$$

- Then, the algebraic equation reads as

$$a_n u_{n-1} + b_n u_n + c_n u_{n+1} = d_n$$

with

$$a_n = -\frac{v\Delta t}{\Delta x}$$

$$b_n = 1 + \frac{v\Delta t}{\Delta x}$$

$$c_n = 0$$

$$d_n = u_n^k + \Delta t f_{n-1}.$$

## Solving a tridiagonal matrix equation

$$\begin{aligned} b_0 u_0 + c_0 u_1 &= d_0 & (i = 0) \\ a_i u_{i-1}^{k+1} + b_i u_i^{k+1} + c_i u_{i+1}^{k+1} &= d_i & (i = 1, \dots, n-1) \\ a_n u_{n-1} + b_n u_n &= d_n & (i = n) \end{aligned}$$

or

$$\begin{bmatrix} b_0 & c_0 & & & & \\ a_1 & b_1 & c_1 & & & \\ & a_2 & b_2 & c_2 & & \\ & & \ddots & \ddots & \ddots & \\ & & & a_{n-1} & b_{n-1} & c_{n-1} \\ & & & & a_n & b_n \end{bmatrix} \begin{bmatrix} u_0 \\ u_1 \\ u_2 \\ \vdots \\ u_{n-1} \\ u_n \end{bmatrix} = \begin{bmatrix} d_0 \\ d_1 \\ d_2 \\ \vdots \\ d_{n-1} \\ d_n \end{bmatrix}$$

- This special linear system can be solved using the **Thomas matrix algorithm**.
- The algorithm is stable for the **diagonally dominant** or **positive definite** matrices.

## Thomas algorithm in Python

```
1  def thomas(a, b, c, d):
2      # Size of the matrix
3      n = len(d)
4      # Calculation of new coefficients
5      c[0] /= b[0]
6      for i in range(1, n - 1):
7          c[i] /= b[i] - a[i]*c[i - 1]
8          d[0] /= b[0]
9      # The forward sweep
10     for i in range(1, n):
11         d[i] = (d[i] - a[i]*d[i - 1])/(b[i] - a[i]*c[i - 1])
12     x = d
13     # The backward sweep
14     for i in reversed(range(0, n - 1)):
15         x[i] -= c[i]*x[i + 1]
16     return x
```

**Listing 1:** Thomas algorithm for tridiagonal matrices

## Transport step in Python

```
1  beta, alpha = v * dt / dx, D * dt / dx**2
2  def transport(u):
3      # Coefficients a, b, c
4      a.fill(-beta - alpha)
5      b.fill(1 + beta + 2*alpha)
6      c.fill(-alpha)
7      # Coefficients a, b, c on the left boundary node
8      a[0] = 0.0
9      b[0] = 1.0
10     c[0] = 0.0
11     # Coefficients a, b, c on the right boundary node
12     a[-1] = -beta
13     b[-1] = 1 + beta
14     c[-1] = 0.0
15     # Dirichlet boundary condition for u on the left boundary node
16     u[0] = ul
17     # Solve the tridiagonal matrix equation
18     thomas(a, b, c, u)
```

Listing 2: Transport step in Python

## **Reactive transport modeling**

---

**Reactive transport in a single fluid phase**

## Reactive transport in a single fluid phase

- Consider a **single fluid phase** with  $N$  chemical species.
- Each species is transported according to the following  $N$  **reactive transport equations**

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{v} - D \nabla n_i) = r_i \quad (i = 1, \dots, N),$$

where

- $n_i$  is the **concentration** of species  $i$  (in  $\text{mol}/\text{m}^3$ );
- $\mathbf{v}$  is the **fluid velocity** (in  $\text{m}/\text{s}$ );
- $D$  is the **diffusion coefficient** of the species (in  $\text{m}^2/\text{s}$ );
- $r_i$  is the **rate of production/consumption** of species  $i$  (in  $\text{mol}/(\text{m}^3 \cdot \text{s})$ ).

## Local chemical equilibrium assumption i

- The **rates of transport** (advection and diffusion) can sometimes be **considerably slower** than the **rates of chemical reactions**.
- **Advection flux rates** are  $n_i v \approx 10^{-5} \text{ mol}/(\text{m}^2 \cdot \text{s})$ , considering  $v \approx 1 \text{ m/day}$ .
- **Diffusion flux rates** are  $-D \nabla n_i \approx 10^{-9} \text{ mol}/(\text{m}^2 \cdot \text{s})$ , considering  $D \approx 10^{-9} \text{ m}^2/\text{s}$ .
- **Rates of aqueous reactions** are several orders of magnitude higher, e.g., the reaction



has a rate of  $r_i \approx 10^{11} \text{ mol}/(\text{m}^3 \cdot \text{s})$ .

- Many aqueous reactions **equilibrate** in the order of microseconds to few seconds!

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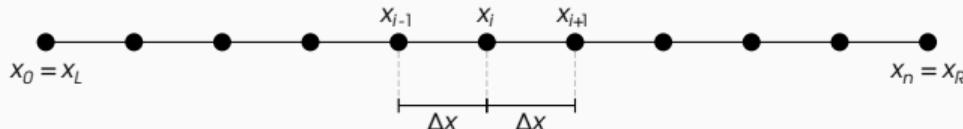


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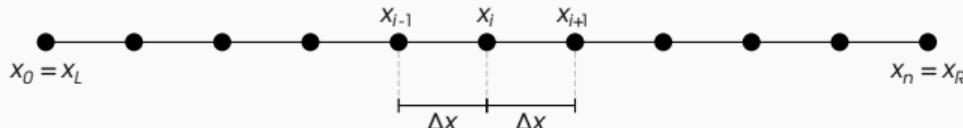
## Local chemical equilibrium assumption ii

- If chemical reactions proceed at a rate much faster than transport rates, we can assume the species react **instantaneously to equilibrium**.
- Then, these chemical species are assumed to be in **local chemical equilibrium** (i.e., at every point in space, they are in chemical equilibrium).
  - As soon as the chemical species are perturbed due to advection and diffusion, they instantaneously react to achieve a new state of equilibrium.
  - For example, as water flows through a reactive porous rock, the fluid gets immediately saturated with the rock minerals.
- We will see that, at every time step, a chemical equilibrium calculation is needed at every node, which could be computationally demanding.



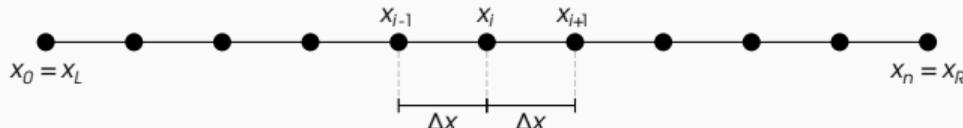
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## Simplifying the reactive transport equations

- We will now simplify the reactive transport equations

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{v} - D \nabla n_i) = r_i \quad (i = 1, \dots, N),$$

using the assumption that the species are in local chemical equilibrium.

- Since the species are in equilibrium at all times, the reaction rates  $r_i$  depend on the rates of transport and cannot be calculated in advance.
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- However, there is a way to **eliminate** them and **drastically reduce the number of transport equations** to solve!

## Things we need in the simplification

- Contribution of each species to the **concentration of element  $j$** :

$$b_j = \sum_{i=1}^N A_{ji} n_i.$$

- **Rate of production of every chemical element** and according to **the mass conservation condition for the elements**:

$$\sum_{i=1}^N A_{ji} r_i = 0.$$

## Reactive transport combined with aqueous-mineral reactions

- We start from the equation for a **single fluid phase**

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{v} - D \nabla n_i) = r_i \quad (i = 1, \dots, N).$$

- If **mineral species** are present, they are **immobile**.
- We **partition the species to fluid and solid species** with corresponding amount of elements  $b^f$  and  $b^s$ , such that the **reactions that occur among aqueous and mineral species** are governed as follows:

$$\frac{\partial n_i^f}{\partial t} + \nabla \cdot (n_i^f \mathbf{v} - D \nabla n_i^f) = r_i^f \quad (i = 1, \dots, N^f),$$

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where superscript s refers to solid, and f to fluid.

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- If **mineral species** are present, they are **immobile**.
- We **partition the species to fluid and solid species** with corresponding amount of elements  $b^f$  and  $b^s$ , such that the **reactions that occur among aqueous and mineral species** are governed as follows:

$$\frac{\partial n_i^f}{\partial t} + \nabla \cdot (n_i^f \mathbf{v} - D \nabla n_i^f) = r_i^f \quad (i = 1, \dots, N^f),$$

$$\frac{\partial n_i^s}{\partial t} = r_i^s \quad (i = 1, \dots, N^s),$$

where superscript s refers to solid, and f to fluid.

## Reactive transport equations in terms of element concentrations

**Exercise:** Using the fact that

$$b_j = b_j^f + b_j^s = \sum_{i=1}^{N^f} A_{ji} n_i + \sum_{i=1}^{N^s} A_{ji} n_i = \sum_{i=1}^N A_{ji} n_i$$

and

$$\sum_{i=1}^N A_{ji} r_i = 0,$$

derive

$$\frac{\partial b_j^s}{\partial t} + \frac{\partial b_j^f}{\partial t} + \nabla \cdot (b_j^f \mathbf{v} - D \nabla b_j^f) = 0 \quad (j = 1, \dots, E).$$

# Reactive transport equations in terms of element concentrations

To solve

$$\frac{\partial b_j^s}{\partial t} + \frac{\partial b_j^f}{\partial t} + \nabla \cdot (b_j^f \mathbf{v} - D \nabla b_j^f) = 0 \quad (j = 1, \dots, E),$$

we use the following **operator splitting** scheme:

- **Step 1:** Ignore the changes in  $b_j^s$  and calculate  $b_j^f$  in every node using

$$\frac{\partial b_j^f}{\partial t} + \nabla \cdot (b_j^f \mathbf{v} - D \nabla b_j^f) = 0 \quad (j = 1, \dots, E).$$

- **Step 2:** Use the updated amounts of elements in the fluid with the elements in the solid to calculate **the amount of elements**  $b_j = b_j^s + b_j^f$ .

**Update the species concentrations**  $n = [n_e, n_k]$ ,  $n_e \in \mathbb{R}^{N_e}$  and  $n_k \in \mathbb{R}^{N_k}$ , calculated at every node

$$\begin{aligned}\frac{db_e}{dt} &= f_e(n_e) & t > 0, & b_e = b_e^o = b_j & t = 0, \\ \frac{dn_k}{dt} &= f_k(n_k) & t > 0, & n_k = n_k^o & t = 0, \\ n_e &= \varphi(T, P, b_e) & t > 0.\end{aligned}$$

# Reactive transport equations in terms of element concentrations

To solve

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## **Reactive transport modeling**

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**Example of reactive transport modeling  
of microbial souring**

# SUBPROBLEMS IN MODELLING THE MICROBIAL SOURING OF WATERFLOODED OIL RESERVOIRS

## Microbial souring

Sulfate reducing bacteria produces H<sub>2</sub>S while growing (the result of metabolic activity)



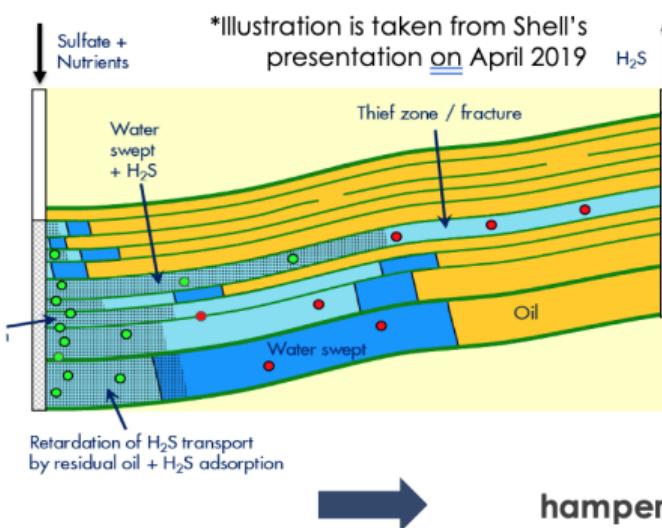
## Hydrogen sulfide (H<sub>2</sub>S) scavenging

'Collection' of the toxic and corrosive H<sub>2</sub>S-gas



## Waterflooding

Injection of the seawater (SW) + nutrients into reservoir with formation water (FW)



hamper the well productivity/injectivity.

Scaled minerals reduce near wellbore permeability and

## Scaling

# MODELLING RESERVOIR SOURING

Injecting water into hydrocarbon reservoirs + exposing fluids to foreign microbes causes **the reservoir souring / increase of H<sub>2</sub>S mass**.

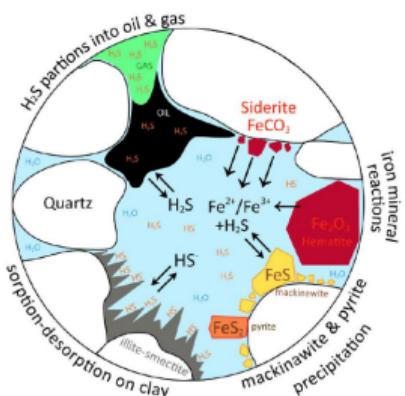


Field level prediction of H<sub>2</sub>S generation and production is important due to

- H<sub>2</sub>S toxicity to human/animals
- H<sub>2</sub>S corrosiveness to most metals causing
  - cracking of drill/transport pipe and tubular goods
  - destruction of testing tools and wire lines

# WHAT IS H<sub>2</sub>S-SCAVENGING?

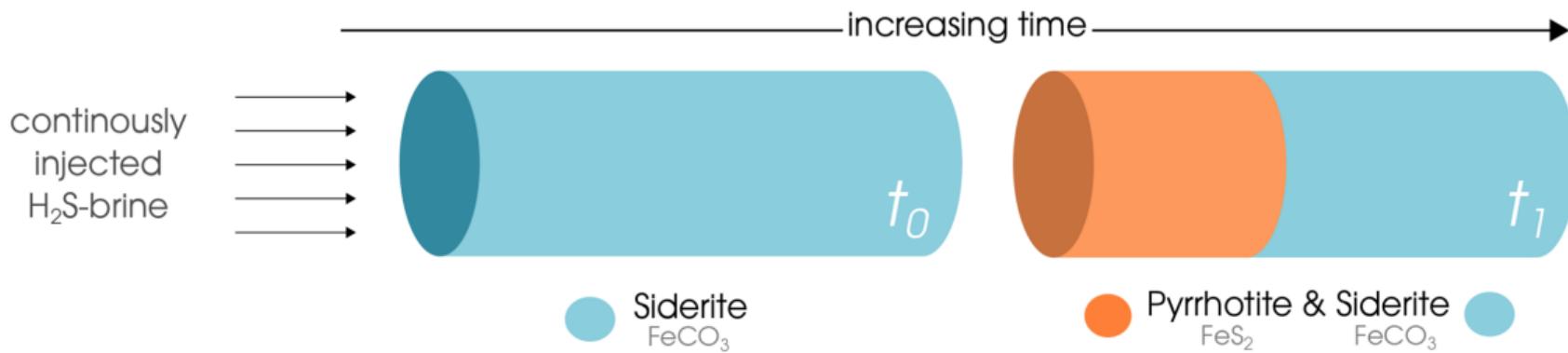
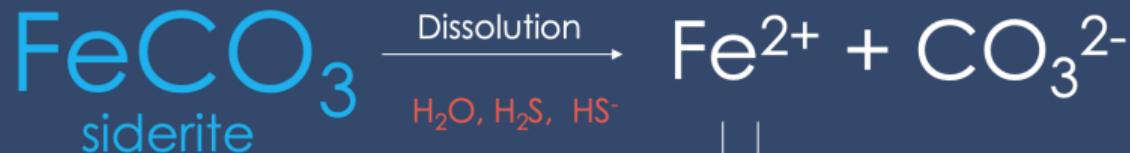
Scavenging is a technique to get rid of hydrogen sulfide.



**Sulfide scavenger** is any chemical that

- **can react** with one or more **sulfide species** (H<sub>2</sub>S, HS<sup>-</sup>, and S<sub>2</sub><sup>-</sup> ect.) and
- **can convert them** to a more **inert form**.

Our scavenger is siderite/iron(II) carbonate (FeCO<sub>3</sub>).



## Discretization Parameters

$\Delta t = 1.2$  hours,  $\Delta x = 1$  m

## Thermodynamic Conditions

$T = 25$  °C,  $P = 1.01325$  bar

## Transport Parameters

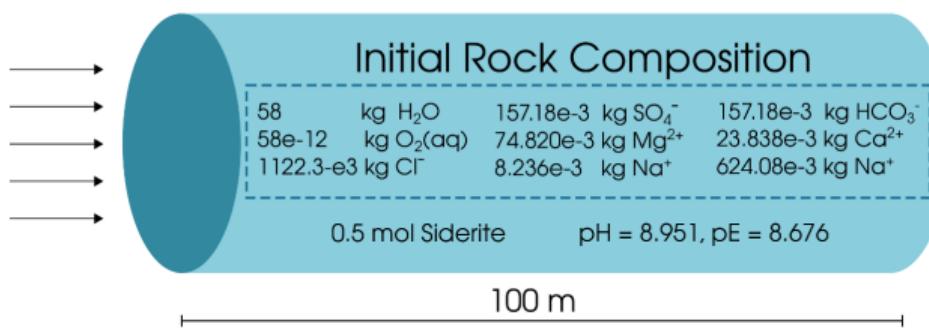
$v = 1.05e-5$  m/s,  $D = 0$

### Injected Fluid Composition

Aqueous species

+

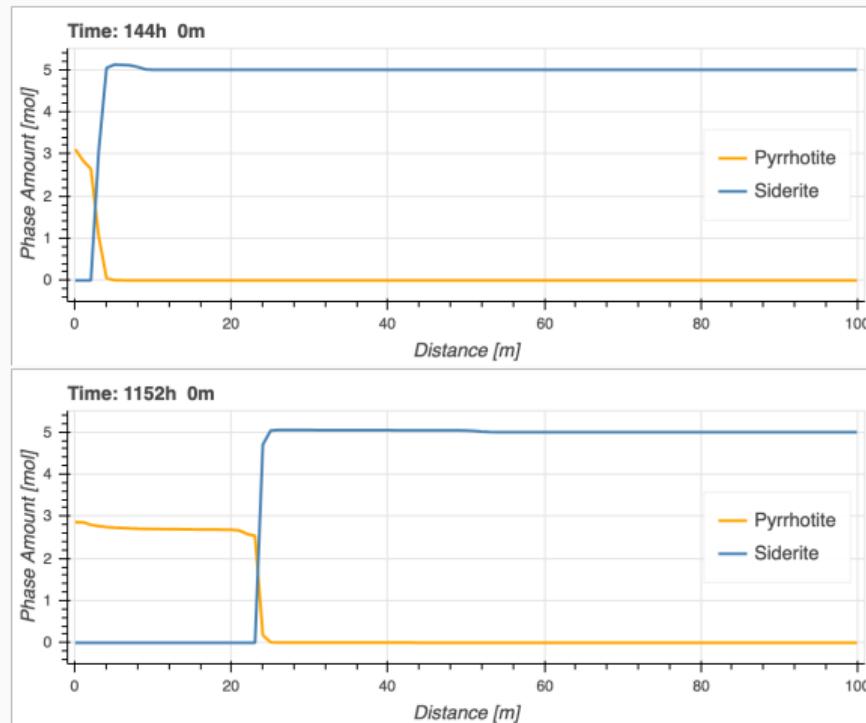
0.0196504 mol HS  
0.167794 mol H<sub>2</sub>S(aq)  
pH = 5.726, pE = 8.220



**Chemical system:** 44 preselected species (incl. minerals) with elements (C, Ca, Cl, Fe, H, K, Mg, Na, O, S)  
**5000 time steps x 100 mesh cells: 500,000 chemical equilibrium calculations**

# Example, Results of souring modeling

Jupyter notebook tutorial *RT modeling of the H<sub>2</sub>S scavenging process along a rock core*:



**Figure 2:** Siderite dissolution and pyrrhotite precipitation.

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