

Reactive Multiphase Flow in Porous Media at the Darcy Scale: a Benchmark proposal

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1 Introduction and context of the proposal

This document presents a proposal for a benchmark on reactive multiphase flow. The proposal was put together as a followup of the first SITRAM meeting <https://sitram19.sciencesconf.org/>, which took place in Pau in December 2019. The topic is increasingly important for modern energy applications.

The content of the benchmark was initially written by SdH and DV, and the current version is the result of discussions between the five authors. The proposal is still work in progress. Preliminary results will be reported by several teams in two sessions of a minisymposium at the upcoming SIAM Conference on Mathematical and Computational Issues in the Geosciences, and it is the organizers' hope that input from the participants will enable the model to be extended towards more realistic geometries as well as physical and chemical phenomena.

A second workshop SITRAM21 will be organized at the end of the year in Paris, where more participants can present results. A special issue of the journal "Computational Geosciences" is planned, where participants can present and compare their work.

The proposal was written to address several challenges commonly met in applications:

1. Robust coupling of chemical reactions with multiphase flow in porous media,
2. Phase behaviour coupling with equilibrium reactions,
3. Conservative treatment of solid phase dissolution and precipitation,
4. Effective coupling of equations in the case of multiple (concurrent) reactions.

The general structure of the physical and chemical model is described in Sections 2 to 5, while the specific data for the proposed cases are given in Section 6.

2 Governing equations

This section briefly covers the governing equations of the multiphase multi-component reactive transport framework for the proposed benchmark study. We start with the basic mass balance equations including the effect of chemical reactions as source/sink term following [Kala and Voskov, 2020]:

$$\frac{\partial n_c}{\partial t} + l_c + q_c = \sum_{k=1}^K v_{ck} r_k^K + \sum_{q=1}^Q v_{cq} r_q^Q, \quad c = 1, \dots, C, \quad (1)$$

where C is a number of species, n_c is the overall mass of component, l_c is the total flux associated with that component, q_c is the total well flow rate associated with that component, v_{ck} is the stoichiometric coefficient associated with kinetic reaction k for the component c and v_{cq} is the stoichiometric coefficient associated with equilibrium reaction q for component c , r_k^K is the rate for kinetic reaction and r_q^Q is the equilibrium reaction rate.

The overall mass of components is defined as

$$n_c = \phi \sum_{j=1}^P (\rho_j s_j x_{cj}) + \sum_{l=1}^M (1 - \phi) \rho_l x_{cl}, \quad c = 1, \dots, C. \quad (2)$$

Here P stands for the total number of fluid phases and M stands for total number of mineral (solid) phases. Here the first term indicates total mass of component c in all the fluid phases whereas the second term is the mass of component c in the solid phases. The term l_c defines the flux of component c and is given as:

$$l_c = \nabla \cdot \sum_{j=1}^P (\rho_j x_{cj} \mathbf{u}_j - \rho_j \phi s_j d_{cj} \nabla x_{cj}), \quad c = 1, \dots, C, \quad (3)$$

where the term d_{cj} corresponds to the dispersion of component c in phase j . The term \mathbf{u}_j is the velocity of the phase j and is defined by Darcy's law:

$$\mathbf{u}_j = -\mathbf{K} \frac{k_{rj}}{\mu_j} (\nabla p - \rho_j g \nabla h) \quad j = 1, \dots, P. \quad (4)$$

Equation 1 can be written in a vector form:

$$\frac{\partial \mathbf{n}}{\partial t} + \mathbf{l} + \mathbf{q} = \mathbf{V}^Q \mathbf{r}^Q + \mathbf{V}^K \mathbf{r}^K, \quad (5)$$

where $\mathbf{n} = (n_1, \dots, n_C)^T$, $\mathbf{l} = (l_1, \dots, l_C)^T$, $\mathbf{q} = (q_1, \dots, q_C)^T$ is the well flow rate, \mathbf{V}^Q and \mathbf{V}^K are the stoichiometric matrix respectively for the equilibrium and kinetic reactions while $\mathbf{r}^Q = (r_1^Q, \dots, r_Q^Q)^T$ and $\mathbf{r}^K = (r_1^K, \dots, r_K^K)^T$ are the equilibrium and kinetic reaction rate vectors.

3 Phase behavior of compositional system

The following equations are used for thermodynamic equilibrium of multicomponent system. A component is in thermodynamic equilibrium if the chemical potential of the components in both phases are equal:

$$f_{c1} - f_{cj} = 0, \quad c = 1, \dots, C, \quad j = 2, \dots, P. \quad (6)$$

The fugacity of a component in a particular phase is given by

$$f_{cj} = \phi_{cj} x_{cj} p, \quad c = 1, \dots, C, \quad j = 1, \dots, P, \quad (7)$$

where ϕ_{cj} is the fugacity coefficient of an ideal mixture. Equation 6 can also be written in terms of the partition coefficients $K_{cj} = \phi_{cj} / \phi_{c1}$:

$$K_{cj} x_{c,1} - x_{cj} = 0, \quad c = 1, \dots, C, \quad j = 2, \dots, P. \quad (8)$$

The system of equations (6) or (8) can be directly coupled with conservation equations (5) and solved in a fully coupled manner using the global Newton solver. Such formulation is often called global or natural formulation. However, when a new phase appears in the process of simulation, the phase equilibrium should be calculated based on the local approximation of the mass from equation (5).

The system of equations can be closed with the following algebraic constraints:

$$\sum_{p=1}^P s_p = 1, \quad (9)$$

and

$$\sum_{c=1}^C x_{cj} = 1, \quad j = 1 \dots, P \quad (10)$$

In case of equilibrium reactions, we need to add the law of mass action to either global or local systems (depends on the preferred nonlinear formulation) which is given as:

$$Q_q - K_q = \prod_{c=1}^C a_{cw}^{v_{cq}} - K_q = 0, \quad q = 1, \dots, Q. \quad (11)$$

Here Q is the number of equilibrium reactions, Q_q is the reaction quotient whereas K_q is the equilibrium reaction quotient or equilibrium solubility limit in case of dissolution/precipitation of minerals, a_{cw} is the activity of the component c in the aqueous phase, and v_{cq} is the reaction stoichiometric coefficient.

4 Porosity treatment

For an accurate treatment of solid phase dissolution and precipitation at the continuous level, the treatment of the rock porosity should be adjusted. Conventionally the control volume (denoted as bulk volume) is subdivided into two regions, void space (occupied by all mobile phases, such as liquid and vapor phase) and solid skeleton (occupied by immobile species, for example, carbonate rock).

In most contributions from the literature, the porosity ϕ depends on the concentrations of the minerals according to the relationship:

$$\phi = 1 - \sum_{m=1}^M \frac{\mathcal{M}_m c_{ms}}{\rho_m}, \quad (12)$$

where M is the number of reactive minerals, \mathcal{M}_m is the molar mass of mineral m , ρ_m is the mass density of mineral m and c_{ms} represents the molar concentration of mineral m .

In the equation (12), it is not clear which properties are spatially correlated and which are changing in time due to dissolution or precipitation reactions. Following the approach suggested in [Farshidi, 2016], we can subdivide the volume of the solid skeleton further into a reactive part which can be modified by chemical reactions and a non-reactive part (which is unaltered by any chemical reaction, and therefore constant throughout the simulation), see Figure 1.

Mathematically this is expressed as follows

$$V_b = V_f + V_r + V_{nr}, \quad (13)$$

and V_r denotes reactive volume and V_{nr} represents the non-reactive volume (not altered by any chemical reaction). Dividing this by the total (bulk) volume gives

$$1 = \phi + \phi_r + \phi_{nr} = \phi^T + \phi_{nr}, \quad (14)$$

where ϕ_r represents the reactive volume fraction, ϕ_{nr} is the non-reactive volume fraction, and ϕ^T is the total porosity defined as the sum of the fluid porosity and reactive volume fraction. Since only the reactive volume and fluid porosity can change due to chemical reactions, it follows directly that the total porosity

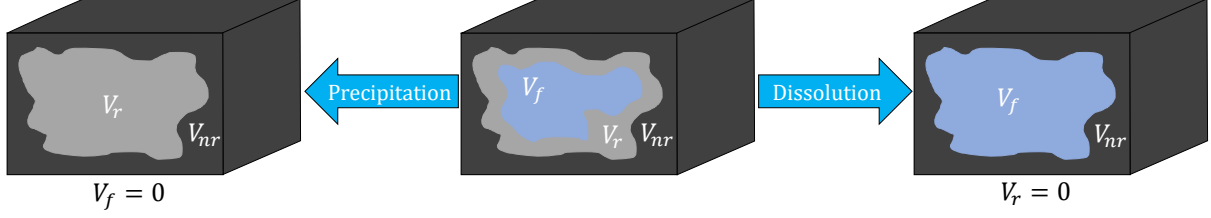


Figure 1: Schematic of the different volumes in the domain. The domain consists of three distinct regions, particularly the fluid volume which is occupied by all the mobile phases (liquid and gaseous in the case of two phase flow), the reactive volume which consists of solid phases that can react or precipitate, and finally the nonreactive volume (the part of the control volume which doesn't participate in any chemical reaction).

remains constant throughout simulation (when neglecting compressibility). This and the changes in volume fractions due to precipitation and dissolution is illustrated in Figure 1.

Note that the fluid porosity can always be obtained with the following constitutive equation

$$\phi = \phi^T \left(1 - \sum_{m=1}^M \hat{s}_m \right), \quad (15)$$

where M is the number of solid phases (occupying the reactive volume fraction) and \hat{s}_m is the saturation of solid phase. Please note that the s_α is the fluid saturation (defined over the pore volume) while \hat{s}_m is the solid saturation of mineral phase m (defined over the pore and reactive rock volume).

Solid saturation in the total porosity formulation can be found with the following equation

$$\hat{s}_m = \frac{V_{r,m}}{V_r + V_f}, \quad (16)$$

where $V_{r,m}$ is the volume of mineral phase m defined as

$$V_{r,m} = \frac{\mathcal{M}_m}{\rho_m} n_m^r, \quad (17)$$

where n_m^r is the total number of moles of mineral m that can participate in any reaction. This means that in the total porosity formulation, the molar concentration of mineral m is defined as

$$\hat{c}_m = \frac{n_m^r}{V_r + V_f}. \quad (18)$$

and since

$$c_{ms} = \frac{n_m^r + n_m^{nr}}{V_b} = \frac{n_m^r}{V_f + V_r} \frac{V_f + V_r}{V_b} + \frac{n_m^{nr}}{V_b} = \hat{c}_m \phi^T + \frac{n_m^{nr}}{V_b}, \quad (19)$$

where n_m^{nr} is the total number of moles of mineral m that cannot participate in any reaction.

The permeability dependence on porosity is approximated using the following power-law equation

$$k = k_0 \left(\frac{\phi}{\phi_0} \right)^A. \quad (20)$$

where k_0 and ϕ_0 are initial porosity and permeability respectively.

5 Additional description for fluid and rock parameters

The relative permeability functions used in this benchmark consist of the Brooks-Corey description, more precisely

$$k_{r,\alpha} = k_{r,\alpha}^e \left(\frac{s_\alpha - s_{r,\alpha}}{1 - \sum_{p \in P} s_{r,p}} \right)^{n_\alpha}, \quad (21)$$

where $k_{r,\alpha}$ is the relative permeability, $k_{r,\alpha}^e$ is the maximum relative permeability, $s_{r,\alpha}$ is the residual saturation, and n_α is the Corey exponent of phase α respectively. In the absence of any residual saturation and $P = \{w, g\}$ (i.e., liquid (water) and vapor (gas) phase present as fluid phases in the system), this results in

$$k_{rw} = k_{rw}^e (s_w)^{n_w}, \quad (22)$$

for the water and

$$k_{rg} = k_{rg}^e (1 - s_w)^{n_g}, \quad (23)$$

for the gas relative permeability.

For the phase density, a simple linear compressibility is assumed, particularly

$$\rho_\alpha = \rho_{\alpha,0} (1 + C_\alpha (p - p_0)). \quad (24)$$

Here C_α is compressibility and $\rho_{\alpha,0}$ is density at pressure p_0 . This is assumed to hold for each of the three phases present in the system, water, gas, and solid. Additional physical complexity can be obtained by adopting a fully compressible model for the gas phase.

We neglect the effect of capillary pressure in this benchmark, hence eq. (3) contains a single pressure.

Table 1 describes how each component distributes over all phases.

Component	Liquid (water)	Vapor (gas)	Solid
H ₂ O	✓	✓	✗
CO ₂	✓	✓	✗
Ca ⁺²	✓	✗	✗
CO ₃ ⁻²	✓	✗	✗
CaCO ₃	✗	✗	✓

Table 1: Component-Phase distribution matrix.

Finally, the activity of each component in the water phase can be written using the following equation

$$a_{cw} = \gamma_{cw} m_{cw}, \quad (25)$$

where γ_{cw} is the activity coefficient and m_{cw} is the molality of component c in the water phase, which in turn can be written as

$$m_{cw} = M_w \left(\frac{x_{cw}}{x_{ww}} \right), \quad (26)$$

where M_w is the moles of H₂O per kilogram of aqueous phase (typically taken as 55.508), x_{cw} is the mole fraction of component c x_{ww} is the mole fraction of H₂O in the aqueous phase respectively. For this benchmark the assumption on an ideal solution is made and hence the activity coefficient is taken as 1.

6 Model setup

The following basic model 1D setup is proposed with injection well (i.e., source term) in the first block and production well in the last block, no flow boundary conditions from left and right (i.e., $\frac{\partial p}{\partial x}|_{x=0} = 0$ and $\frac{\partial p}{\partial x}|_{x=\Delta x N_x} = 0$). These are typical reservoir simulation type of boundary conditions. It is possible to replace the wells and no-flow boundary condition with a Neumann boundary condition at $x = 0$ and a Dirichlet at $x = \Delta x N_x$ (with the values for volumetric rate, injection stream, and pressure as found in Table 3).

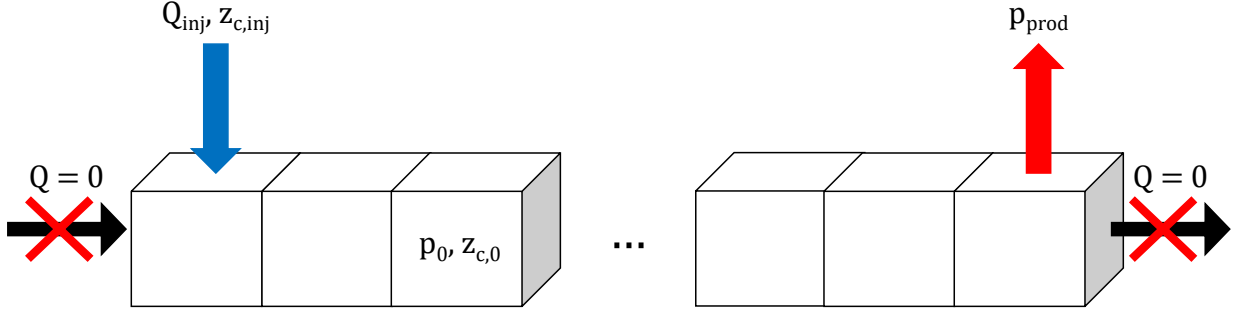


Figure 2: One dimensional domain setup. Injection on the left is constrained with rate and composition Q_{inj} and $z_{c,inj}$ respectively. Production on the right is constrained with pressure p_{prod} . Initial condition for pressure and composition is defined as p_0 and $z_{c,0}$ respectively. No flow boundary condition is imposed on both the left and right boundary.

The rock and fluid related parameters are shown in the Table 2.

Property	Value	Units
Permeability, $k_{x,y,z}$	[100, 100, 100]	[mD]
Total porosity, ϕ^T	1	[-]
Control volume dimension, $\Delta x, y, z$	[1, 1, 1]	[m]
Number of control volumes, N_x	1000	[-]
Phase density, $\rho_{w,g,s}$	[1000, 100, 2000]	[kg/m ³]
Phase compressibility, $C_{w,g,s}$	[1e-6, 1e-4, 1e-7]	[1/bar]
Phase viscosity, $\mu_{w,g}$	[1, 0.1]	[cP]
End-point relative permeability, $k_{rw,rg}^e$	[1, 1]	[-]
Corey exponents, $n_{w,g}$	[2, 2]	[-]
Residual saturation, $s_{rw,rg}$	[0, 0]	[-]
Phase partition coefficients, K_{H_2O,CO_2}	[0.1, 10]	[-]
Diffusion coefficients, $d_{c_j} = d$	1e-9	[m ² /s]
Activity coefficients, $\gamma_{cw} = \gamma$	1	[-]
Porosity-permeability dependence factor, A	3	[-]

Table 2: Values for all the relevant fluid and rock properties.

6.1 Two-phase flow with kinetic chemistry

The first test case consists of a two-phase flow problem with a single kinetic chemical reaction (i.e., we cannot reduce the global system of nonlinear equation using the element reduction). The system consists of the following components: $z_c = [\text{H}_2\text{O}, \text{CO}_2, \text{Ca}^{+2}, \text{CO}_3^{-2}, \text{CaCO}_3]$. The kinetic reaction equation consists of



The kinetic rate (i.e., the right-hand-side of equation 5) is written as

$$r_k = AK_k \left(1 - \frac{Q}{K_{sp}} \right) \quad (28)$$

where A is the reactive surface area which is a linear function of the solid saturation ($A = A_0 \hat{s}_s = (1 - \phi_0) \hat{s}_s$), K_k is the kinetic reaction constant, Q is the activity product (to simplify $Q = x_{ca,w} \times x_{co3,w}$) and K_{sp} is the equilibrium constant.

The following Table 3 summarizes the initial, injection and production conditions, simulation time, and kinetic constant.

Property	Value	Units
Injection rate, Q_{inj}	0.2	[m ³ /day]
Injection composition, $z_{c,inj}$, $c = 1, \dots, C - 1$,	[0, 1, 0, 0]	[-]
Initial pressure, P_{ini}	95	[bar]
Initial composition, $z_{c,ini}$, $c = 1, \dots, C - 1$,	[0.15, 0, 0.075, 0.075]	[-]
Production pressure, P_{prod}	50	[bar]
Simulation time, T	1000	[days]
Kinetic constant, K_k	1	[-]
Solubility constant, K_{sp}	0.0625	[-]

Table 3: Boundary conditions and other simulation parameters.

Note that composition for the C -th component can be obtained by $z_C = 1 - \sum_{j=1}^{C-1} z_j$ and is not a primary unknown (hence the initial and injection composition doesn't contain the composition of z_C), are primary unknowns in this system are $X = [p, z_1, \dots, z_{C-1}]$. K_{sp} is equal to $0.25 \times 0.25 = 0.0625$ to ensure that the initial state is in equilibrium and no dissolution occurs.

A Python code will be provided to make it easier to express the boundary conditions in terms of concentrations of individual species for those codes that may need it. Alternatively, the initial and injection composition expressed in terms of molar fraction of individual species and saturation of each phases are given in section 8.

6.2 Two-phase flow with equilibrium chemistry

The second test case is similar to the first one, except that now the reaction is treated as an equilibrium reaction. Mathematically, this adds an additional constraint equation of the form

$$Q - K_{sp} = 0, \quad (29)$$

where Q is the activity product of the equilibrium reaction as defined in equation (11) (which is taken here to have the same form as in Section 6.1) and K_{sp} is the solubility constant, with the value given in Table 3.

All the other parameters, fluid/rock/boundary condition/simulation parameters (as specified in table 2 and 3), are the same as the previous example (including of course the stoichiometry of the reaction).

6.3 Extended chemical system

The described chemical systems (both equilibrium and kinetic) can be complemented by additional reactions. Specifically, we propose the following two equilibrium reactions:



and



with equilibrium constant K_w and $K_{b\text{icarb}}$ respectively.

Please note that this increases the total number of species by three, particularly to $z_c = [\text{H}_2\text{O}, \text{CO}_2, \text{Ca}^{+2}, \text{CO}_3^{-2}, \text{H}^+, \text{OH}^-, \text{HCO}_3^-, \text{CaCO}_3]$. However, this allows to represent the CaCO_3 reaction (eq. (28)) in a more generic way with dependency on the pH of the solution (i.e., depend on the $-\log_{10}(a_{\text{H}^+})$). For example, the kinetic rate in eq. (28) can be represented as

$$r_k = K_1 x_{\text{H},w} + K_2 x_{\text{CO}_2,w} + AK_3 \left(1 - \frac{Q}{K_{sp}}\right), \quad (32)$$

where $K_{1,2,3}$ are specific reaction rate constants for each of the reaction-steps.

7 Expected output

The expected output for the test-case specified in section 6.1 is shown on Figure 3 hereafter.

8 Appendix

Properties based on injection state: state = [P, z_h2o, z_co2, z_ca, z_co3]

Injection state = [1.65e+02 1.00e-12 1.00e+00 1.00e-12 1.00e-12]

	H2O	CO2	Ca+2	CO3-2	CaCO3
Composition, z_c	1.00e-12	1.00e+00	1.00e-12	1.00e-12	1.00e-12
Liquid MoleFrac	1.00e-11	1.00e-02	4.94e-01	4.94e-01	0.00e+00
Vapor MoleFrac	1.00e-12	1.00e+00	4.94e-13	4.94e-13	0.00e+00
Solid MoleFrac	0.00e+00	0.00e+00	0.00e+00	0.00e+00	1.00e+00

	Liquid	Vapor	Solid
Phase MoleFrac	1.02e-12	1.00e+00	1.00e-12
Mass Density	1.00e+03	1.01e+02	2.00e+03
Viscosity	1.00e+00	1.00e-01	0.00e+00
Sat. phi_tot	1.17e-13	1.00e+00	1.00e-12
Sat. phi_fluid	1.17e-13	1.00e+00	0.00e+00

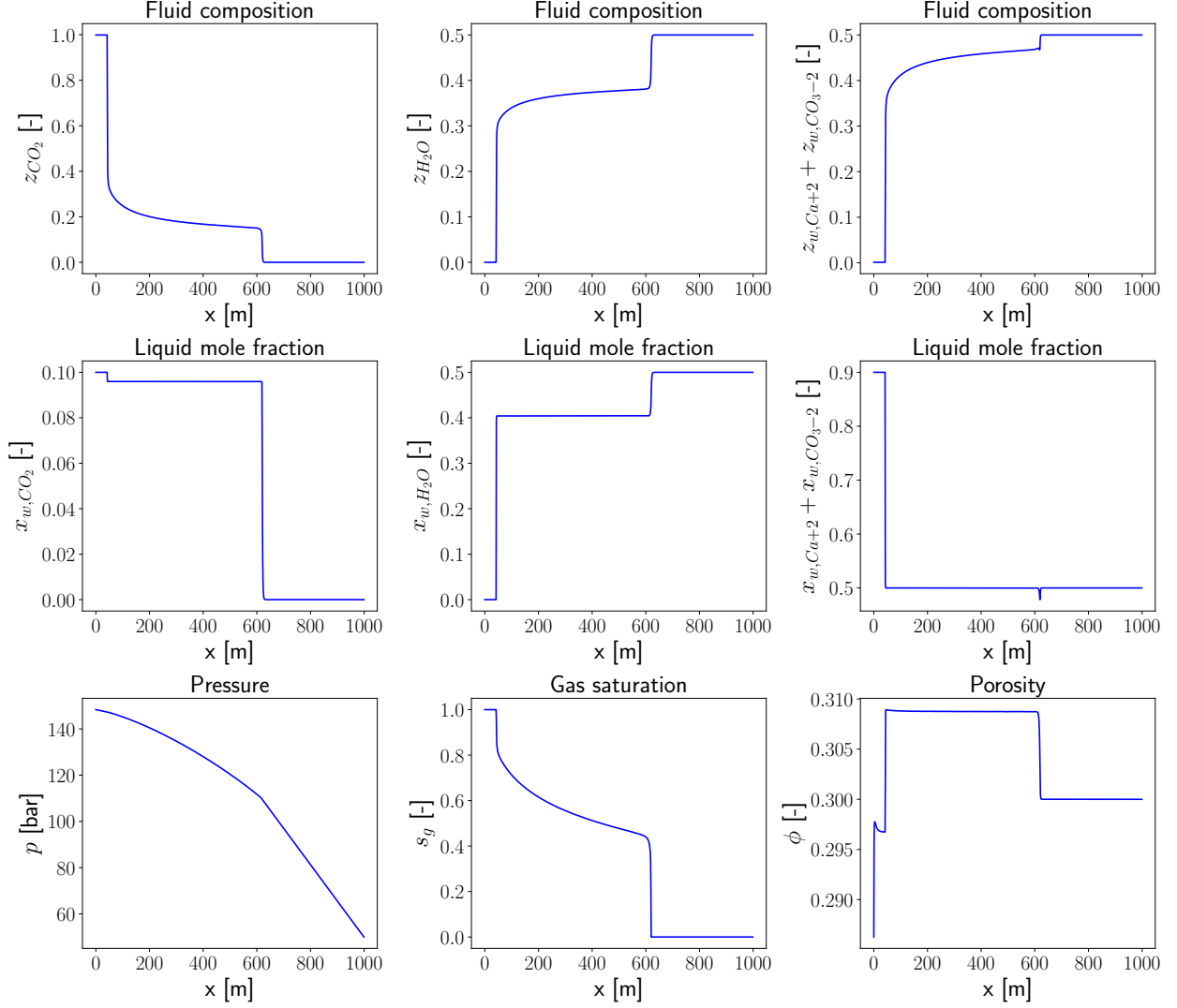


Figure 3: In the initial stage, due to the absence of ions in the injection stream, dissolution of the $CaCO_3$ occurs, since the solution is under-saturated. However, the vaporization of the H_2O due to the CO_2 injection causes precipitation to occur, hence the porosity reduces close to the injection point (left boundary).

Properties based on initial state: state = [P, z_h2o, z_co2, z_ca, z_co3]
Initial state = [9.5e+01 1.5e-01 1.0e-12 7.5e-02 7.5e-02]

	H2O	CO2	Ca+2	CO3-2	CaCO3
Composition, z_c	1.50e-01	1.00e-12	7.50e-02	7.50e-02	7.00e-01
Liquid MoleFrac	5.00e-01	3.33e-12	2.50e-01	2.50e-01	0.00e+00
Vapor MoleFrac	5.00e-01	3.33e-12	2.50e-01	2.50e-01	0.00e+00
Solid MoleFrac	0.00e+00	0.00e+00	0.00e+00	0.00e+00	1.00e+00

	Liquid	Vapor	Solid
Phase MoleFrac	3.00e-01	0.00e+00	7.00e-01
Mass Density	1.00e+03	1.00e+02	2.00e+03
Viscosity	1.00e+00	1.00e-01	0.00e+00
Sat. phi_tot	3.00e-01	0.00e+00	7.00e-01
Sat. phi_fluid	1.00e+00	0.00e+00	0.00e+00

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