Document Version
Final published version

Citation (APA)
Lu, J., Voskov, D., & Novikov, A. (2025). *Modeling of irreversible thermodynamics relevant to CCS using parameterization approach*. Paper presented at 6th EAGE Global Energy Transition Conference and Exhibition , Rotterdam, Netherlands. https://doi.org/10.3997/2214-4609.202521034

Modeling of irreversible thermodynamics relevant to CCS using parameterization approach

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Summary

This work presents an extension of the Operator-Based Linearization (OBL) framework to model irreversible thermodynamic behavior in geological carbon storage (CCS). Traditional OBL employs adaptive parameterization over primary state variables (pressure, temperature, and composition) but lacks the ability to represent hysteresis phenomena critical to CO_2–brine systems. To address this, we introduce an additional state parameter—the historical maximum gas saturation into the OBL operator space, enabling accurate modeling of hysteresis in relative permeability and capillary pressure.

The extended framework is validated through a series of numerical tests. A single-cell simulation demonstrates how Land–Killough hysteresis formulations capture saturation-path-dependent permeability behavior. A 2D aquifer model further illustrates improved CO_2 trapping and sharper plume fronts due to hysteresis effects. Finally, we apply the model to the heterogeneous SPE11 benchmark, showing enhanced capillary trapping and reduced dissolution under realistic subsurface conditions.

This approach allows for the rigorous integration of irreversible physics into adaptive interpolation without altering the solver structure. Future work includes incorporating capillary pressure hysteresis, validating against field-scale simulators, and extending to fully implicit formulations.

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Introduction

Carbon Capture and Storage (CCS) in deep saline aquifers involves complex thermodynamic behavior driven by fluid displacement and entrapment. These processes often become irreversible due to hysteresis in multiphase flow properties, particularly relative permeability and capillary pressure. Accurate modeling of such irreversible phenomena is critical for predicting long-term storage security, plume evolution, and injection performance (Krevor et al. 2015).

Voskov (2017) proposed Operator-Based Linearization (OBL), which offers a computationally efficient approach by converting nonlinear physical behaviors into multidimensional interpolation tables through adaptive parameterization (Khait and Voskov, 2018). Within this framework, governing equations are reformulated as state-dependent operators, with the operator space fully determined by the current thermodynamic state. The Open Delft Advanced Research Terra Simulator (Voskov et al., 2024), an open-source software built on the OBL methodology, demonstrates the effectiveness of the approach across a range of carbon capture and storage (CCS) applications (Lyu et al., 2021; Lyu and Voskov, 2023; Wapperom et al., 2024). However, conventional OBL used in the open-DARTS framework assumes reversible thermodynamics and therefore cannot capture the hysteresis effects frequently observed in CCS processes.

To address this, we propose an extension of the OBL method by incorporating irreversible state variables (e.g., maximum gas saturation) directly into the adaptive parameterization framework of open-DARTS. This enhancement allows for a more accurate and physically consistent representation of irreversible thermodynamics and hysteresis within the OBL approach, specifically tailored to the challenges of CCS modeling. The results are demonstrated for two realistic CCS problems.

Method and Theory

Here we briefly describe the OBL approach based on mass conservation. In overall molar formulation, the primary unknowns are pressure (p) and composition (z_c), which define the thermodynamic state ω of the problem. The mass conservation, neglecting the source term, can be rewritten as the component of a residual vector in an algebraic form:

$$r_c(\xi, \omega) = a(\xi)\alpha_c(\omega) + \beta_c(\omega)b(\xi, \omega) = 0 \quad (1)$$

where ξ represents the spatial state, which is fixed in the calculation. Instead of evaluating complex physical functions and their derivatives directly in simulation, OBL adaptively generates multidimensional interpolation tables for accumulations (α_c) and flux (β_c) operators as functions of thermodynamic state. A detailed description can be found in Voskov (2017).

In this study, we propose an extension of the original OBL methodology where an additional irreversibility parameter (ψ) is added to the physical state $\hat{\omega}$, and the Eq.(1) can be written as:

$$r_c(\xi, \hat{\omega}) = a(\xi)\alpha_c(\hat{\omega}) + \beta_c(\hat{\omega})b(\xi, \hat{\omega}) = 0 \quad (2)$$

Where $\hat{\omega} = \{\omega, \psi\}$and $\psi = f(\omega_n, \omega_{n-1})$. Here, *n* and *n-1* are the current and previous timesteps, respectively. This treatment makes the time approximation explicit with respect to ψ.

After iteration converged for each timestep, there is a hysteresis computation for every reservoir cell to achieve the transition between the drainage and imbibition curve while hysteresis occurs. The main steps of hysteresis computation are shown in Algorithm 1.

The extended OBL framework involves:

- **Adding of irreversible parameter:** Introducing historical maximum gas saturation (S_{gmax}) as an additional state/dimension that parameterizes the irreversible hysteresis effects.

- **Adaptive operator interpolation:** On-the-fly parametrization and interpolation of operators in multidimensional state space to capture irreversible transitions efficiently.

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Algorithm 1: Computation of hysteresis
Input: $S_g^n, S_g^{n-1}, S_{gmax}^n$
/* Transition from drainage curve to imbibition curve*/
if $S_{gmax}^n$ and $S_g^n < S_g^{n-1}$:
    $S_{gmax}^{n+1}$
    $k_{rg}^{n+1} = k_{rg}^{n+1}(S_g^{n+1}, S_{g\max}^{n+1})$
/* Transition from imbibition curve to drainage curve */
else if $S_{gmax}^n$, $S_g^n > S_g^{n-1}$ and $S_g^n >= S_{gmax}^n$:
    $S_{gmax}^{n+1}$
    $k_{rg}^{n+1} = k_{rg}^{n+1}(S_g^{n+1}, S_{gmax}^{n+1})$
```

Examples

Preliminary numerical studies using the relative permeability hysteresis example. The hysteresis model proposed by Killough (1976) is employed to construct the imbibition scanning curves from primary drainage curves, capturing irreversibility through a parametric interpolation, which was proved more accurate in the prediction of hysteresis effect on relative permeability in gas-water system (Foroudi et al.2022).

We conducted a single-cell numerical test incorporating relative permeability hysteresis. In our setup, we manually prescribed a drainage–imbibition cycle by varying the CO_2 composition to first increase and then decrease, thereby mimicking injection followed by brine re-entry. The historical maximum gas saturation (S_{gmax}) was dynamically tracked and used to define the branch (drainage or imbibition) during hysteresis computation.

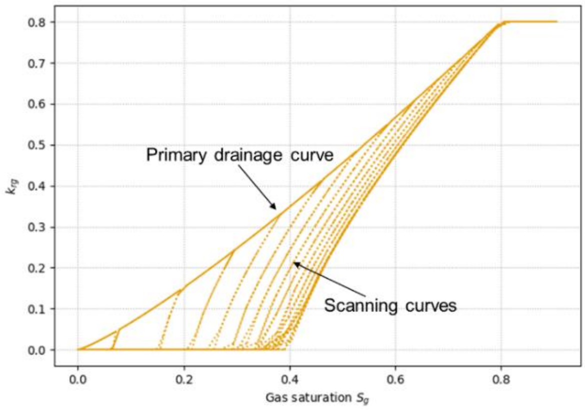

Fig.1 *Relative permeability change in drainage and imbibition processes using Killough's model .*

The resulting hysteresis loop in gas relative permeability is shown in Fig. 1, clearly demonstrating the transition between drainage and imbibition with the residual trapping behaviour introduced by hysteresis. This confirms that Algorithm 1 can successfully encode relative permeability hysteresis calculation.

To assess the impact of the extended OBL parametrization framework on field-scale behaviour, we simulated a 2D (100m×50m) aquifer model with initial residual gas saturation of 0.1 and maximum residual gas saturation of 0.4. The scenario represents a full-cycle CO_2 injection and post-injection migration scenario over 100 years, with 3 years of active CO_2 injection followed by 97 years of passive plume evolution.

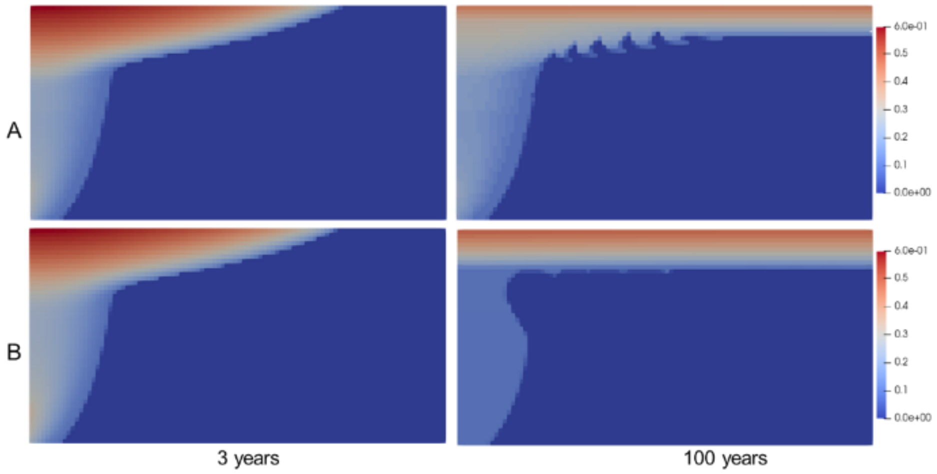

Fig.2 *Gas phase saturation profile in a 2D homogeneous model. (A) and (B) present results obtained using the original OBL formulation and the extended OBL model, respectively.*

Fig.2 compares the gas saturation distributions obtained using the extended OBL model-A with the added irreversible hysteresis parameter S_{gmax} and the original OBL model-B based only on primary state variables. Model A demonstrates significantly more CO_2 trapping within the brine, owing to the embedded hysteresis logic. The extended model successfully captures irreversible thermodynamic effects, such as increased residual trapping due to hysteresis, reduced post-injection gas mobility, and sharper and more localized CO_2 fronts.

To further evaluate the capability of the extended OBL model in a realistic and heterogeneous setting, we applied it to the SPE11 benchmark reservoir (Hadjisotiriou et al., 2025). The model was initialized with a residual gas saturation of 0.1 and a maximum residual gas saturation of 0.2, using a relatively coarse grid with a resolution of 210 cells in the horizontal (x) direction and 30 cells in the vertical (z) direction. The simulation was run for 100 years.

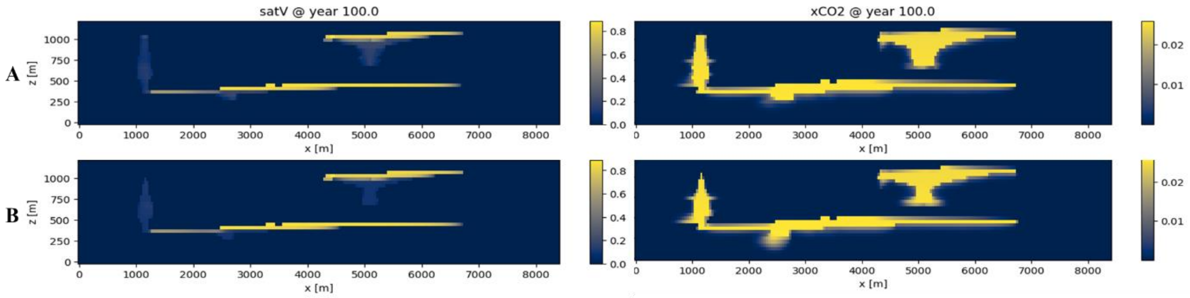

Fig.3 *Gas phase saturation(satV) and CO_2 dissolution (xCO_2) profile in SPE11 model. (A) and (B) present results obtained using the original OBL formulation and the extended OBL model respectively*

As illustrated in Fig. 3, the simulation incorporating the hysteresis model predicts increased CO_2 residual trapping and decreased CO_2 dissolution compared to the non-hysteretic model. This demonstrates the model's capability to capture irreversible flow behaviour in highly heterogeneous media with realistic physical processes. However, it is important to note that the current simulation does not account for the long-term dynamics of the system, during which gravity-driven instabilities can significantly enhance CO_2 dissolution and potentially diminish the impact of hysteresis (Wang et al., 2022).

Conclusions

The developed parametrization approach within the Operator-Based Linearization framework successfully models irreversible thermodynamics in realistic CCS scenarios by explicitly employing a history-dependent irreversible parameter in hysteresis calculation. By integrating Killough hysteresis models, the method enables accurate representation of relative permeability hysteresis within full-cycle CO_2 injection and migration simulations.

Future work includes the validation of the extended model against commercial simulators in large-scale reservoir scenarios. Besides, we are going to integrate capillary-pressure hysteresis and expand the implementation to support fully implicit formulations of hysteresis-aware thermodynamic calculations. That will enable tighter coupling between physics and numerical stability for field-scale applications and allow us to investigate the long-term effects of hysteresis on CO_2 trapping.

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