Final Technical Report

DOE Award Number: DE-SC0019075

Awardee/Institution Name: Stanford University

Period of Performance: 08/01/2018 - 07/31/2023

PI Name: Ilenia Battiato, PhD

Project title: Multiscale Dynamics of Reactive Fronts in the Subsurface

Abstract

Understanding and predicting flow and reactive transport in rocks (i.e. geologic porous media) is critical to many technologies at the heart of the energy transition, including CO_2 sequestration and H2 storage. However, accurate modeling and prediction of these systems is very complex because physico-chemical processes that occur at very small spatial scales, i.e. in the pores of the rocks, can dramatically control the system performance at the field scale (km). For example, precipitation reactions at the pore-scale can lead to large permeability changes at the field scale and dramatically alter the migration of stored gases. Properly accounting for multi-scale coupling effects is critical to achieve predictivity and confidence in model outputs, which then can guide design and optimization at the system-scale. This can be achieved through the development of rigorous mathematical models that can appropriately account for fine-scale effects at the large scale. The final report of the Early Career award DE-SC0019075 "Multiscale dynamics of reactive fronts in the subsurface" summarizes the mathematical, numerical and experimental advancements to study and predict reactive transport in geologic porous media across scales.

We emphasize that the grant was transferred to Stanford on 08/01/2018 from San Diego State University, where it was awarded in 2015. So, while this final report needs to cover the period 08/01/2018-07/31/2023, for completeness we will include the totality of the science produced under this grant for its entire duration.

Goals

The goals of this grant were to advance the basic science necessary to properly understand, model and predict reactive, multiphase flows in geologic porous and fractured media, while accounting for scale effects. Also, because of the basic science nature of this research, we demonstrated transferability and translation of the discoveries to other fields/systems important to the geosciences. The methods used to advance these goals have involved theoretical, numerical and experimental methods and techniques outlined below.

<u>Major Experimental Activities [4,12,19]</u>: Our activities have involved the investigation of 3 critical complementary aspects characterizing reactive transport in geologic media: (1) the presence of fractures and mass and momentum fluxes (and their modeling) at the fracture matrix interface [4]; (2) time varying boundary chemical conditions [12] and (3) the impact that multiphase flow (and gas generation) has on effective reaction rates [19]. We investigate this in turn.

(i) *Understanding transport in hyperporous fractured systems*

We have developed a set of microfluidic fracture-matrix systems where we systematically investigated the impact of matrix permeability on solute transport. We demonstrate that matrix permeability cannot be neglected when studying mass transport in fractures. This has important implications when studying transport in carbonate rocks, where fractures may be embedded in hyperporous matrices as a result of cement dissolution processes. We have also developed and validated continuum-scale models and demonstrated how parameter-free forward predictions in well-controlled systems can be developed by combining pore-scale and continuum-scale models.

(ii) *Development of Lego-Fluidics: building blocks for spatio-temporal micro-environment control*

One main focus of this research effort is to shed light on the impact that temporal fluctuations in input signals, e.g. concentration, have on transport processes and reactions at the continuum scale. Most active microfluidic devices that create concentration variation do so by either active or passive mechanisms. In the first case, they modify the flow field; in the second case, passive micro-structures with premixing chambers have been used for generating time varying signals which are structure-specific. These techniques either do not allow one to disentangle the impact of the time-varying flow field from that of mass transport or are not flexible enough to explore the parameter space in terms of signal frequency, amplitude etc. (since one device has to be built for each signal). A major progress we have made in this reporting period consists in the design, development and testing what we refer to as Lego-Fluidics, i.e. the building blocks of a microfluidic system that allow one to generate arbitrarily complex time-varying signals without changing the microchannel structure. This is achieved through a systems of carefully designed gas-valves. The system has been developed to specifically investigate passive and reactive transport in fracture matrix systems (resembling flow in idealized fractured carbonate rocks). Figure 1 shows a sketch of the design and a picture of the device developed at the Stanford Nanofabrication Facility. We believe this system will have a broad impact not only on the study of temporally varying signals for geoscience applications, but also in other lab-on-a-chip systems in the context of drug delivery, bioreactors etc., due to its robustness and precision.

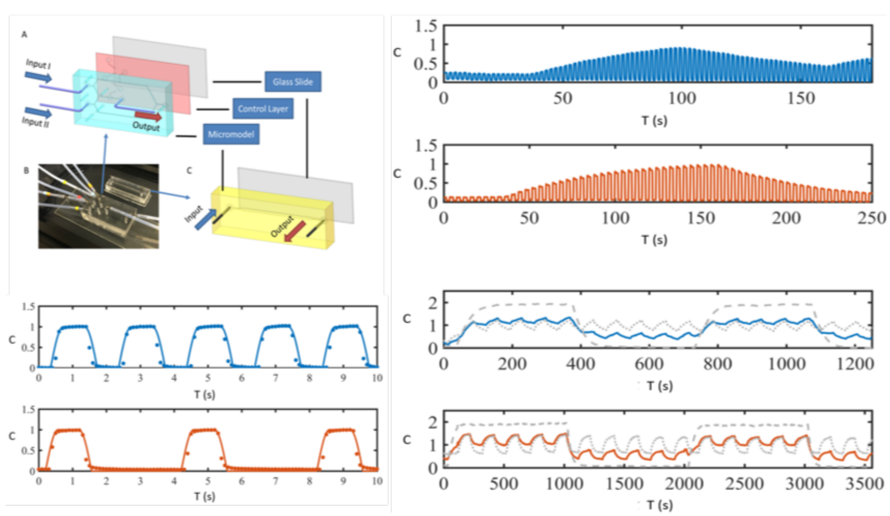

Figure 1: Lego-Fluidic Design Prototype and example of temporally varying signals generated. Signals with different characteristic time scales, both slow and fast, can be created [12].

(iii) *Gas shielding effect in multiphase reactive flow in porous* media

In multiphase systems, gas bubbles can obstruct reactions between the liquid phase and solid boundaries by shielding the reactive surface. We developed an analytical model that quantifies this slowdown by establishing a relationship between the reaction rate and gas saturation, incorporating a fitting parameter. we perform reactive microfluidic experiments on carbonate-rich rocks using hydrochloric acid. We leverage machine learning-based image analysis to derive the relationship directly from the images. Our findings show good agreement between the experimentally observed relationship and our analytical predictions ($S_g^{1/2}$ scaling relationship). This relationship is also applicable to a broader range of systems beyond carbonate dissolution.

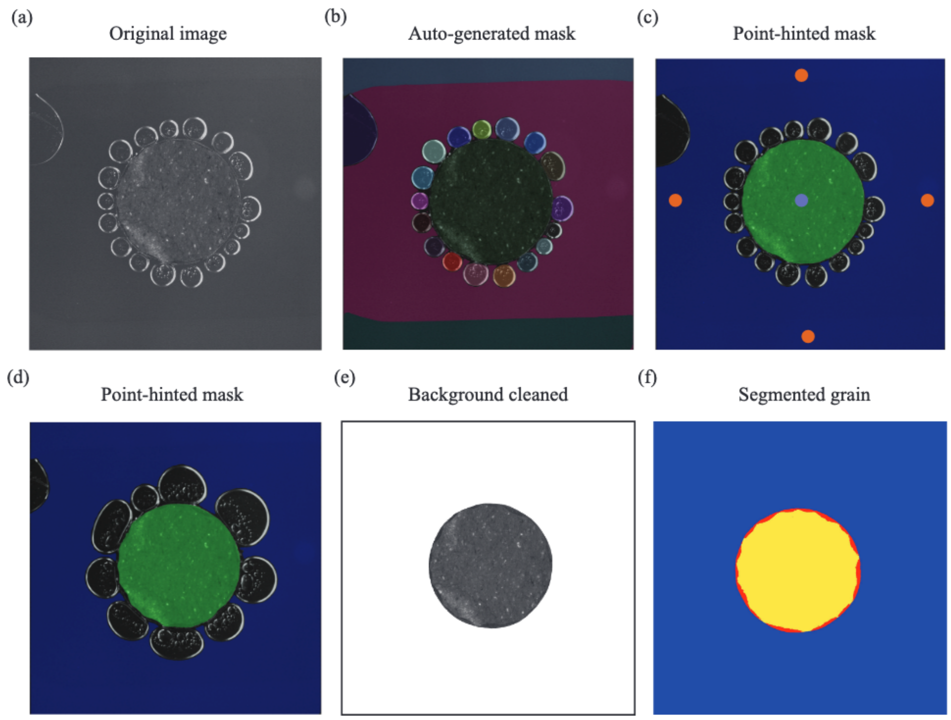

Figure 2: (a) Original image from the dissolution experiment (b) Auto-generated masks for bubbles overlayed on the original image (c) Point-hinted masks overlayed on the original image. Four points for the background are specified and one point for grain is specified. (d) Point-hinted masks (e) Original image with background cleaned (f) Segmented grain by new protocol

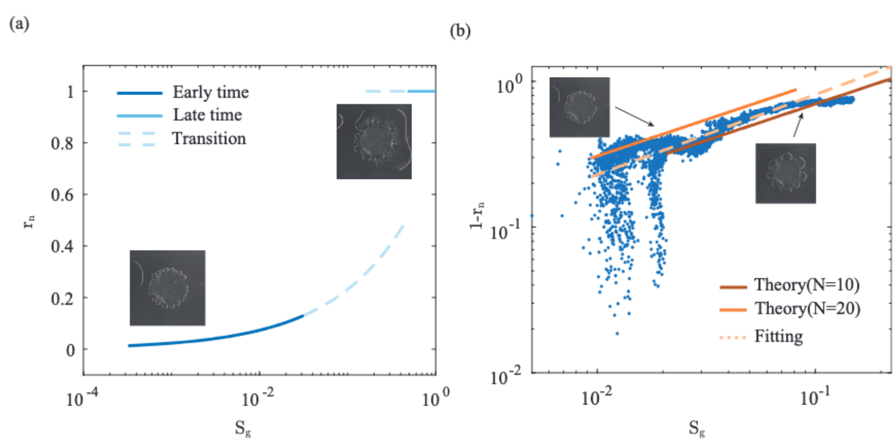

Figure 3: (a) Model theoretical results (b) Experimental results

Major Numerical Activities [3,8,13,15,16,17,18,20]: Our effort have spanned the development of numerical scheme to appropriately model precipitation dissolution processes [3,8,15] as well as the use of ML strategies for model parametrization [13,18]. Particularly notable is the development of novel computer algebra structures that enables the full automation of symbolic deductive procedures to derive upscale models by multiple scale expansions [16,17,19,20].

(i) *Development of Immerse-Boundary Methods to model reactive transport in porous media*

An important component of our efforts is to develop computational tools to model reactive transport in time-evolving porous media. Immerse Boundary methods represent an attractive option since it is based on cartesian grids, which are easy to generate, while they exhibit great resilience in handling complex geometries. Yet, most of the numerical discretization schemes in IBM are developed to handle Dirichlet boundary conditions (typical of heat transfer problems). We have developed a novel high order ghost-cell IBM to account for all types of boundary conditions including Neuman and Robin, critical in reactive transport problems.

(ii) *Use of ML techniques to estimate effective parameters of porous media*.

In a series of works, we have demonstrated how CNN combined with homogenization theory can significantly speed up the estimation of effective parameters in Darcy-scale models. Understanding the transport properties of fluids through porous media is crucial in a wide range of scientific and engineering applications. Accurately predicting key parameters, such as permeability and effective dispersion, is essential for optimizing these processes. These parameters depend not only on the pore-scale geometry but also on flow conditions, and are traditionally expensive to compute since they are generally determined by solving direct numerical simulations on macroscopic pore- scale domains. Such computational costs limit the effectiveness of data-driven approaches in terms both of predictive accuracy and/or types of geometries that can be accurately handled. This is because the computational cost for training over a broad set of topologies and dynamic conditions is prohibitive. In this work, we propose an approach that combines deep learning with multiscale modeling techniques, and exploit the computational efficiency of homogenization theory to support a data-driven technique. By using only a representative unit cell for training purposes, we are able to generate a large dataset of porous media images and corresponding permeability and dispersion tensors at a significantly reduced computational cost, while spanning an unprecedented range of the geometric and dynamic parameter space (See Figure 4). The dataset is composed of 10,000 images, is designed to include a wide variety of morphological properties and serves as the training set for a Convolutional Neural Network (CNN) that estimates permeability and dispersion tensors from both microstructural images and input flow conditions described by the Peclet number (see Figure 5). The CNN can quickly and accurately characterize effective properties (permeability and dispersion coefficients) spanning more than three orders of magnitude for a wide range of pore-scale topologies and flow regimes (See figure 6). These results highlight the potential to enhance porous media characterization and prediction in various fields.

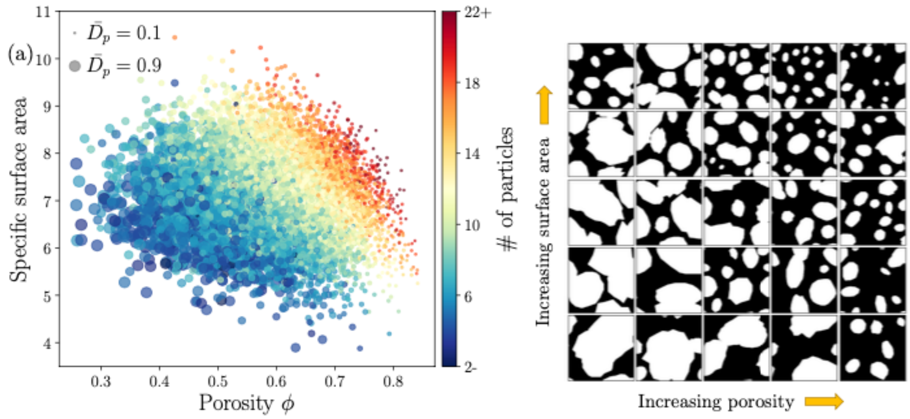

Figure 4: Scatter plot depicting porosity and specific surface area – normalized by the side length of the unit cell 30 – for each of the 10,000 images generated. The color coding represents the number of particles in the unit cell while the size of the datapoint corresponds to the average particle diameter in the unit cell. (b) Example images from the dataset showing the broad range of morphologies considered

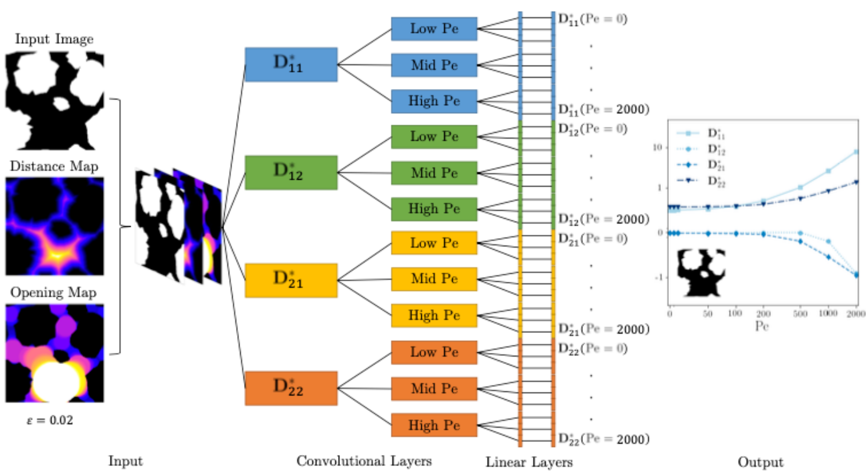

Figure 5: Diagram of the proposed CNN for dispersion prediction. The CNN takes a binary image as an input, makes the desired transformations, then branches into predicting the full dispersion tensor for Pe = 0 through Pe = 2000.

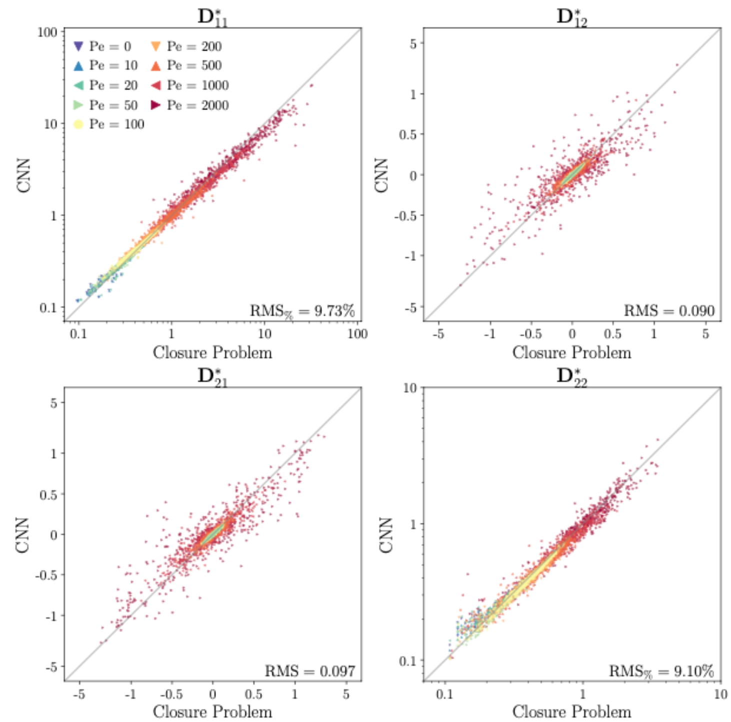

Figure 6: CNN results on the validation set for predicting the components of the dispersion tensor for all Peclet numbers. The CNN results shown are for the network with both the distance and opening map included.

(iii) Development of the first symbolic deduction software able to automatically perform sophisticated applied mathematical derivation for scale-translation.

One of the critical features of reactive transport in geologic porous media is that complexity is not a tuning parameter: reactions can follow complex reaction networks with many species involved, homogeneous and heterogenous reactions happening concurrently, multiple mineral surfaces etc. The rigorous upscaling of such systems has been historically prohibitive, with the outcome that mathematical upscaling theories would be only applied to toy problems or setups with limited complexity. As such, the benefits of these approaches (i.e. a priori known error bounds on upscaled models) could not permeate to the modeling of systems with realistic complexity. We have developed a new computer algebra algorithm that has enabled to full automation of homogenization technique by multiple scale expansions through symbolic deduction. The symbolic deductive engine we created, called Symbolica, has sped up mathematical derivations (generally performed by humans) by 5 orders of magnitude (from month/years to seconds/minutes) and has allowed us to rigorously derive models at the Darcy scale (and with the accuracy prescribed by homogenization theory) systems of unprecedented complexity (20 species, multiple mineral reactive surfaces, etc) in few minutes. The same calculations would have been impossible to carry by hand. Our results have attracted a lot of attention in the scientific community and we believe they will lead to a paradigm shift in modeling reactive transport in geologic media. We have also proposed the first Symbolic-Numeric framework where we can derive and numerically implement (i.e. write codes) models automatically with minimal human input.

Major Theory Development Activities [2,5,6,7,9,11,19]: Nearly all the activities outlined above include advancements in theory that were necessary to push methods and basic understanding forward. Here we mention few additional topics.

(i) Studying the impact of flow regimes on the upscaling of multiphase flow

Another major effort in this reporting period has focused on the development of upscaled models for multiphase flow in porous media, while accounting for the topology of the flowing phases. Although recently recognized both experimentally and numerically, the topology of the flowing phases is not taken into account in classical Darcy-type equations. We upscale the multiphase Navier-Stokes equations to the continuum scale while taking into account pore-scale flow regimes, e.g. slug flow, connected pathways etc. We also apply the approach to flow in a capillary tube, determine analytical expressions for the relative permeability of the wetting and nonwetting phases in different flow regimes and demonstrate that the effect of the flowing-phases topology on the relative permeabilities is significant. We finally extend our scaling laws to transport in complex porous media (Figure 7) and validate our findings against both experimental data and numerical simulations as shown in Figure 8.

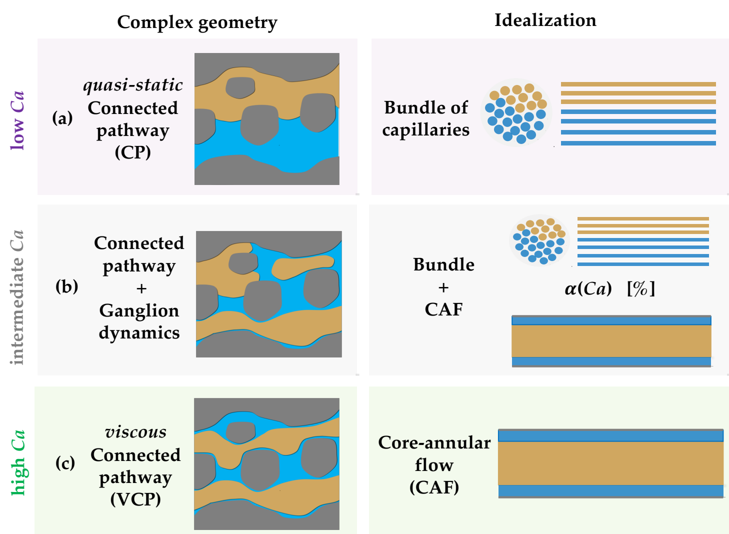

Figure 7. Flow regimes and capillary tube conceptualization

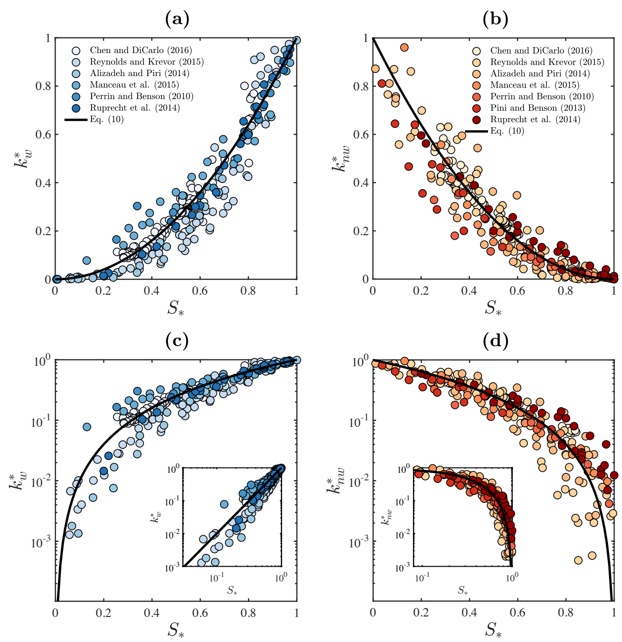

Figure 8: Scaling laws for relative permeabilities

(ii) Studying the impact of multiphase flow on dissolution reactions

As discussed already in the experimental section, we have also developed models to correlate reaction rates to multiphase flow.

Translation to other fields [1,10,14]: Our efforts have demonstrated that basic science discoveries can be ubiquitously applied to advance different fields. In a series of works we have applied the theories/methods developed for reactive transport in geologic media to advance other domains' knowledge. Some examples include the study of flow and transport over canopies [1] and predicting effective properties of battery porous electrodes [10,14].

References

1. S. Rubol, Battiato, I., De Barros, F., 'Vertical dispersion in obstructed shear flows', Water Resour. Res., (2016).

2. S. Korneev, Battiato, I., 'Sequential homogenization of reactive transport in polydisperse porous media', SIAM Multiscale Model. Sim., 14, 4, pp. 1301-1318 (2016)

3. Korneev, S., Xiaofan, Y., Zachara, J., Scheibe, T. D., Battiato, I., 'Method of segmentation with downscaling for unresolved images of a highly heterogeneous porous sample', Water Resour. Res., 54, WR022886 (2018).

4. B. Ling, Oostrom, M., Tartakovsky, A. M., Battiato, I., 'Hydrodynamic dispersion in thin porous channels with controlled microtexture', Phys. Fluids, 30, 076601, Editor's Pick (2018)

5. D. Picchi, Battiato, I. 'The impact of pore-scale flow regimes on upscaling of immiscible two-phase flow in porous media', Water Resour. Res. 54 (9), pp. 6683-6707, (2018).

6. Battiato, I., D. O' Malley, C. T. Miller, P. S. Takhar, F. Valdes-Parada, B. D. Wood, 'Theory and applications of macroscopic models in porous media', Transp. Porous Med., 13 (1) pp. 1-72, (2019).

7. D. Picchi, Battiato, I., 'Relative permeability scaling from pore-scale flow regimes', Water Resour. Res., 55 (4), pp. 3215-3233 (2019).

8. M. Yousefzadeh, Battiato, I., 'High order ghost-cell immersed boundary method for generalized boundary conditions', Int. J. Heat Mass Tran., 137, (2019).

9. D. Picchi, Battiato, I., 'Scaling of water-steam relative permeability and thermal fluxes in geothermal reservoirs', Volume 129, 103257, Int. J. Multiphase Flow (2020)

10. S. Korneev, H. Arunachalam, S. Onori, Battiato, I., 'A data-driven multiscale framework to estimate effective properties of lithium-ion batteries from microstructure images', 134:173–194, Transport Porous Med. (2020).

11. D. Picchi, J. Suckale, Battiato I., 'Taylor drop in a closed vertical pipe', J. Fluid Mech. (2020).

12. B. Ling, I. Battiato, 'Module-fluidics: Building blocks for spatio-temporal micro-environment control', 13(5), 774, Micromachines, (2022)

13. R. M. Weber, S. Korneev, I. Battiato, 'Homogenization-Informed Convolutional Neural Networks for Estimation of Li-ion Battery Effective Properties', Transp Porous Med 145, 527–548, (2022)

14. Weber, R.; Korneev, S.; Battiato, I., 'Labeled Image Dataset of Generated Porous Electrode Microstructures and Calculated Transport Parameters for Neural Network Training', Mendeley Data, V1, (2022).

15. M. Yousefzadeh, Y. Yao, I. Battiato, `A level-set immersed boundary method for reactive transport in complex topologies with moving interfaces', J. Comp. Phys., Volume 478, 2023, 111958, (2023)

16. Pietrzyk, K., Battiato, I., 'Automated Symbolic Upscaling: 2. Model Generation for Extended Applicability Regimes', 59, 7, e2023WR034894, Water Resour. Res. (2023)

17. Pietrzyk, K., Battiato, I., 'Automated Symbolic Upscaling: 1. Model Generation for Extended Applicability Regimes', 59, 7, e2022WR033600, Water Resour. Res. (2023).

18. R. Weber, I. Battiato, "Homogenization-informed Convolutional Neural Network to Predict Permeability and Dispersion in Porous Media", Submitted to Adv. Water Resour., ADWR-D-24-00745 (2024).

19. S. Yu, Battiato, I., "Gas shielding effect in multiphase reactive flow in porous media" To be submitted to Phys. Rev. Lett., (2024).

20. K. Pietrzyk, I. Battiato, "Symbolic Deduction in Computational Physics", To be submitted to SIAM Reviews, (2024).