Coupled mass transfer processes during underground hydrogen storage

Investigators:
PI: Anna Herring, Department of Civil and Environmental Engineering, University of Tennessee, Knoxville
Email: aherri18@utk.edu
PI: Haochen Li, Department of Civil and Environmental Engineering, University of Tennessee, Knoxville

Primary GE^2-relevant research focus: energy storage

1. Overview and Summary

Hydrogen fuel is proposed as an approach to mitigate the intermittent nature and seasonal fluctuations of renewables-based energy production. However, high-capacity and long-term storage options for hydrogen do not exist. Underground hydrogen storage (UHS) in porous rock formations could be a reliable and cost-effective method to solve storage issues and enable hydrogen to be used to balance energy supply and demand. However, for UHS to succeed, research is needed to determine how to easily and safely inject then recover H_2 in a repetitive cyclic scheme. Once injected underground, H_2 gas will flow through the irregular porous architecture of the host rock, in competition and along with the resident aqueous phase, creating a complex multiphase system. The fluid distributions (and resulting flow properties) are controlled by a suite of physio-chemical factors and are not reversible but are strongly hysteretic. Predictions of H_2 transport are further complicated by its relatively low density, low solubility, and very high diffusivity compared to other reservoir-relevant fluids (e.g. oil, methane, CO_2), and conventional understanding of mass transfer processes for multiphase fluids in porous media are severely deficient with respect to H_2 storage. This project will elucidate the physio-chemical dynamics of coupled mass transfer processes for hydrogen gas stored in porous geologic reservoirs - fundamental processes that must be constrained to establish safe and efficient deployment of UHS operations. If feasible, this technology would provide a major breakthrough, accelerating the urgently needed energy transition.

2. Research Description and Objectives

Three physio-chemical mass transfer mechanisms must be considered in predicting the efficiency of cyclic H_2 injection-recovery processes: 1) capillary trapping and displacement of the bulk gaseous phase, 2) dissolution, and 3) diffusion. Capillary trapping is physical phenomena where small bubbles or “ganglia" of gas are held within pore spaces of the storage rock via interfacial forces; capillary trapping is known to immobilize a significant fraction of nonwetting fluid in a multiphase system, however, these ganglia may be subsequently mobilized by viscous or buoyant forcing. Dissolution of H_2 into the reservoir groundwater is a chemical process driven by bombardment of the H_2 molecules by the aqueous solvent, resulting in mass transfer of H_2 from the gaseous phase into the resident groundwater. Diffusion drives dissolved H_2 molecules through the aqueous phase from high to low concentrations, further dispersing the H_2 and potentially accelerating dissolution. Dissolution and diffusion may induce physical changes in the size and morphology of H_2 ganglia, with resulting impacts to the stability and distribution of capillary trapped H_2 (we have made similar observations for CO_2-water-sandstone systems). The relevant time scales, length scales, and inter-dependencies of these three mechanisms must be constrained. This knowledge, combined with other requisite knowledge gains in microbial and geochemical interactions, and transient flow processes, is needed to obtain accurate predictions of injected H_2 behavior in the subsurface and design of safe storage operations. Ultimately, we will determine ***dynamic microstructure-fluid property-mass transfer relationships*** to predict the relative importance of the three mass transport processes via four sequential objectives:

1. Determine dissolution-displacement and diffusion-displacement couplings (including structural and chemical criteria, and relevant time scales) via novel 4D Planar Laser Induced Fluorescence (PLIF) and particle image velocimetry (PIV) pore-scale imaging experiments.
2. Isolate and quantify the individual impact of structural and fluid property contributions via experiment-validated pore-scale higher-fidelity computational fluid dynamics (CFD) simulations; and extend simulations to high pressure and temperature conditions relevant to H_2-reservoir systems and larger length scales.
3. Conduct dynamic reservoir condition experiments in geologic samples, utilizing 4D synchrotron x-ray imaging to validate and enhance the CFD model for larger scales and realistic storage media.
4. Integrate these experimental and modeling efforts to derive new mathematical models and dimensionless parameters describing the dynamics and coupling of displacement, dissolution, and diffusion mass transfer mechanisms across time and length scales.

GE^2 seed funding will be used to validate our experimental and computational approach; i.e. demonstrate proof-of-concept of objectives (1) and (2). A validated approach will be the foundation for multiple proposals to the DoE and NSF that extend these objectives and address objectives (3) and (4).

3. Expected Significance and Potential

The proposed research centers on **long-term, high-capacity energy storage** and aligns with critical national interests in mitigating climate change as represented in the 2021 Bipartisan Infrastructure Deal and the 2022 Inflation Reduction Act. The research is similarly well-aligned with the mission and goals of the GE^2 initiative, targeting the Grand Challenges of *pioneering future fuels such as hydrogen adoption, generation, and storage* and *spearheading the development of renewable and affordable energy solutions for a sustainable future* through the development of large scale, economically efficient hydrogen storage. If successful, the proposed work will produce the fundamental knowledge needed to deploy efficient and safe UHS that would enable advances in climate change mitigation and adaption technologies. It builds innovative and interdisciplinary tools to advance understanding of multiphase gas-water flows in porous systems that are relevant to other engineered processes including hydrogen electrolysis and carbon capture and storage operations. The preliminary research enabled by a GE^2 award will elucidate and establish foundational understanding of coupled mass transport processes and provide evidence for feasibility of our proposed approach. The results of these proof-of-concept experiments will be published in high-impact journals, e.g. *Environmental Science & Technology*, *Nature Communications*, or *Physical Review Letters*.

4. Plans for Pursuing External Funding Support

A GE^2 seed award will be used to accomplish three objectives: (1) establish experimental capability, (2) demonstrate proof of concept to maximize probability of external funding success, and (3) launch a productive UTK-based collaboration, establishing UTK as a key player and initiating up a robust research future in this new field.

First, given the real and perceived risks associated with working with gaseous H_2, we need to proactively establish the capability to safely conduct experiments; this will include conducting risk analyses, establishing protocols, and obtaining approvals from UTK EHS. We are in communication with other groups at UTK who conduct experiments with H_2 gas (Prof. Doug Aaaron in MABE), as well as Prof. Kamaljit Singh, who is leading UHS studies at Heriot Watt University in the UK. We will use knowledge from those teams to ensure a safe and economically efficient execution in preparations to work with H_2.

Second, the data acquired from our first experiments will demonstrate proof of concept of the methods as well as demonstrate to external funding sources that we have the capability to conduct the additional studies needed to fully explore the proposed research project. The topic represents a high value opportunity as the extended project has strong fundamental and applied aspects relevant to multiple external funding agencies. This project directly targets hydrogen cost reduction goals of the Hydrogen Earthshot energy storage program Long Duration Storage established by the DoE Office of Energy Efficiency & Renewable Energy (EERE). Thus, the first full proposal developed from the seed award will target the use-inspired funding opportunities at the DoE. We anticipate proposing a $1,100,000 project to EREE. The basic research aspects of this work aligns well with multiple NSF program priorities within the Chemical, Bioengineering, Environmental, and Transport Systems (CBET) Division and the Hydrologic Sciences program within the Division of Earth Sciences. Thus, the second full proposal will target the basic research aspects of the multiphase fluid dynamics, and we anticipate proposing a $700,000 project by July 2024.

Finally, GE^2 funding will provide a platform for two Assistant Professors with complementary expertise to launch a strong collaborative group in an up-and-coming research topic with huge potential for growth. Although UHS is new new research topic for both PIs, the research is a natural extension of the team's expertise. PI Herring has extensive experience in designing and implementing experiments of multiphase fluid flows in porous media under high pressure, high temperature conditions representative of geologic storage reservoirs, and in the use of X-ray imaging to characterize these systems. PI Li is a fluid mechanician who develops the sophisticated computational tools necessary to simulate such complex multiphase processes, and also operates and maintains the laser system that underlies the first experimental component of the project. Once the concept is demonstrated and fully funded, the two PIs plan to establish a joint research group focusing on UHS and the dynamics of multiphase fluids in porous media, initiating a robust research future in UHS and related climate change adaption technologies. Eventually, we anticipate that this group will grow within UTK, developing a strong national and international collaborative network, and will be a source of continuous (and increasing) funding.

5. Proposed Research and Methods

Specific aim 1: Determine dissolution-displacement and diffusion-displacement couplings (including structural and chemical criteria, and relevant time scales) via novel 4D Planar Laser Induced Fluorescence (PLIF) and Particle Image Velocimetry (PIV) pore-scale imaging experiments.

The GE^2 seed will be used to fund the first type of experiments targeting dissolution-displacement processes, to establish proof-of-concept. These experiments will utilize laser fluorescence to visualize concentration and water velocity

gradients surrounding capillary trapped H_2 bubbles in transparent porous media (i.e. porous hydrogel with identical refractive index to water). Dissolution of H_2 into water will induce a change in solution pH as some H_2 dissociates to H^+, this process can be precisely monitored using pH-fluorescent indicators (we have identified three options: Thermo Fisher pHrodo Green, pHrodo Red, and carboxy SNARF™-1). To investigate dissolution-displacement linkages, we will place a H_2 bubble within clean (non-H_2-saturated) water-filled transparent media. A double-pulsed Nd: YAG laser system (Litron, Springfield, MA) will be utilized to create a thin laser sheet that excites fluorescent indicators in a horizontal plane across the H_2 bubble. An optical filter with a cutting-off wavelength of 550 nm is used to filter the original laser light wavelength of 532 nm and preserve the fluorescence wavelength (e.g., typically 580 nm and 640 nm for carboxy SNARF™-1 dye). A high-resolution CMOS camera (12 million pixels) with a Tokina at-X PRO M 100mm F2.8 D Macro Lens (i.e., field view of 1 cm$\times$1 cm) will be used to focus on the H_2 bubble at the laser sheet's normal angle and capture a sequence of images of subsequent dissolution (via pH evolution) and displacement (via bubble deformation and movement) processes. Bubble microstructure (including volume, interfacial area, and interface curvatures indicative of capillary pressure) and locations will be monitored continuously.

Specific aim 2: Isolate and quantify the individual impact of structural and fluid property contributions via experiment-validated pore-scale higher-fidelity computational fluid dynamics (CFD) simulations; and extend simulations to high pressure and temperature conditions relevant to H_2-reservoir systems and larger length scales.

Utilizing the OpenFOAM framework, an open-source finite volume method (FVM), we will develop a CFD simulation with enhanced accuracy to model the H_2 mass transfer process at the pore scale. To track the dissolution interface between the H_2 and aqueous phase, we will employ the volume of fluid (VOF) method. Minimizing numerical diffusion at the dissolution interface will be achieved through the utilization of a multidimensional limiter for explicit solution (MULES) method with interface compression interfacial method. A well-balanced numerical scheme will be developed to accurately capture the influence of surface tension. Additionally, to account for the presence of granular media, non-penetration boundary conditions will be directly incorporated. Our initial step involves utilizing the developed CFD model to simulate bench-scale PLIF and PIV experiments. The H_2 dissolution rate will be parameterized based on the empirical data. Numerical convergence analysis will be performed to ensure sufficient computational resolution to resolve the bubble mass transfer dynamics. We will then compare the simulation results with the experimental data to evaluate the accuracy of the CFD model in predicting flow statistics and mass transfer dynamics. Detailed analysis will be devoted to elucidating the fundamental mechanism that controls the stability of H_2 gas bubbles in a porous media.

Once experimental method and CFD model are validated, we will extend the experiments and CFD model to assess impacts of diffusion in addition to dissolution, and both these processes impacts to bubble stability across a wide range of structural and fluid properties under in-situ conditions, targetting increasing pressure and temperature. Our specific objective is to investigate scaling effects, aiming to establish a comprehensive relationship that connects the pore-scale dynamics with behavior relevant to the reservoir scale.

6. Timeline and Benchmarks

These proposed research activities will be carried out for **12-month project duration**, beginning in August 2023. The **specific milestones** and outcomes are shown below.