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Review

A Comprehensive Review of Biogeochemical Modeling of Underground Hydrogen Storage: A Step Forward in Achieving a Multi-Scale Approach

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Abstract: This paper presents an in-depth investigation of the biogeochemical modeling approaches applied to underground hydrogen storage. It delves into the intricate dynamics of hydrogen in the subsurface, focusing on small (pore-lab scale) and reservoir-scale models, highlighting the importance of capturing microbial, geochemical, and fluid flow dynamic interactions in porous media to simulate storage performance accurately. Small-scale models offer detailed insights into localized phenomena, such as microbial hydrogen consumption and mineral reactions, and can be verified and calibrated against laboratory data. Conversely, large-scale models are essential to assess the feasibility of a project and forecast the storage performance, but cannot be proven by real data yet. This work addresses the challenge of transitioning from fine-scale to reservoir models, integrating spatial heterogeneity and long-term dynamics while retaining biogeochemical complexity. Through the use of several simulation tools, like PHREEQC, Comsol, DuMuX, Eclipse, CMG-GEM, and others, this study explores how modeling approaches are evolving to incorporate multiphysics processes and biochemical feedback loops, which are essential for predicting hydrogen retention, flow, and potential risks. The findings highlight the strengths and limitations of current modeling techniques and suggest a workflow for exploiting at best existing modeling capabilities and developing reservoir models to support hydrogen storage appraisal and management.

Keywords: underground hydrogen storage; biogeochemical modeling; reservoir simulation; multiphysics simulation; scale transition modeling

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1. Introduction

Underground hydrogen storage (UHS) is gaining increasing attention as a solution to balance energy supply and demand in a sustainable energy future [1,2]. Underground hydrogen storage represents a promising solution for large-scale energy storage, playing a critical role in achieving energy transition goals [3]. This process involves the injection and retrieval of hydrogen gas into subsurface geological formations such as saline aquifers, depleted oil and gas reservoirs, and caverns [4–6]. While UHS offers significant potential, its effectiveness and safety are heavily influenced by complex biogeochemical interactions that occur within the storage medium [7,8].

These interactions arise from the interplay between microbial activity, geochemical reactions, and fluid dynamics. Indigenous microorganisms in the reservoir can metabolize hydrogen, altering its composition and generating byproducts such as methane and hydrogen sulfide (H_2S) [9]. These byproducts pose risks to the integrity and efficiency of the storage system, potentially reducing the purity of the hydrogen and leading to operational challenges. Concurrently, geochemical reactions between hydrogen and reservoir minerals can induce changes in critical properties such as porosity and permeability [10,11]. These changes directly impact gas flow, storage efficiency, and reservoir stability over time. The long-term success of UHS depends on understanding and managing these biogeochemical processes to ensure the stability of the stored hydrogen and the operational safety of the reservoir.

However, the successful implementation of UHS requires a detailed understanding of the complex physical, chemical, and biological processes that occur in the subsurface [12]. Accurate modeling of these processes is essential for predicting the long-term behavior of hydrogen, evaluating storage efficiency, and identifying potential risks such as gas loss, contamination, or changes in reservoir properties or caprock sealing capacity [11,13,14]. Models allow us to simulate the movement, distribution, and transformation of hydrogen in reservoirs and evaluate the efficiency of storage operations as well as potential risks [12,15]. Models can be divided into several key categories: *compositional models*, which focus on fluid-phase behavior in the reservoir; *fluid dynamic models*, which describe fluid flow in porous media; *geo-mechanical models*, which assess the mechanical integrity of the reservoir and caprock; and *geochemical models*, which analyze the chemical interactions between hydrogen, minerals, and formation fluids [3,16–21].

In addition, an increasingly important aspect is the modeling of microbial activity, which accounts for the impact of microorganisms on hydrogen quality and quantity [9,15]. Methanogens, acetogens, sulfate-reducing bacteria, and iron-reducing bacteria can significantly alter the chemical environment of the storage site by consuming hydrogen and producing gases like methane (CH_4), hydrogen sulfide (H_2S), ferrous iron (Fe^{2+}), and acid compounds (as acetate) in the liquid phase, thus inducing reservoir souring and causing corrosion of the storage infrastructure [9,12]. In particular, methanogens convert hydrogen and carbon dioxide into methane, thus reducing the amount of hydrogen available in storage, while sulfate-reducing bacteria (SRBs) consume hydrogen and sulfate to produce H_2S, a corrosive and toxic gas that can compromise the safety of the storage facility [22]. Iron-reducing bacteria (FeRBs) interact with hydrogen to reduce ferric iron to ferrous iron, altering the geochemistry of the storage site [23]. In parallel, geochemical reactions such as the dissolution of sulfates and the release of carbonate ions into the formation water provide nutrients for microbial communities [24]. The precipitation of minerals such as siderite ($FeCO_3$) or pyrite (FeS_2) further alters the reservoir chemical environment, affecting both microbial activity and hydrogen retention [17,23]. Because all the microbial activities are influenced by the availability of substrates such as hydrogen, sulfate, and carbon sources (as carbonates and CO_2), the electron acceptor (like ferric iron) concentration, and the geochemical composition of the reservoir rock and water, it is essential to integrate biological reactions together with geochemistry into the modeling framework [3]. Furthermore, the ability of microbes to thrive in different subsurface conditions (namely, temperature, pressure, pH) requires detailed modeling to predict how the microbial metabolism will evolve during hydrogen storage [25,26]. Another related concept is “Gold Hydrogen”, where microbial activities in suitable reservoirs facilitate the in situ production of hydrogen [27]. In these systems, fermentative bacteria and methanogens metabolize residual hydrocarbons or organic compounds, generating hydrogen directly within the storage site [28]. While this process can enhance sustainability by reducing the reliance on surface injections, it also introduces challenges, such as hydrogen consumption by competing microbial pathways or contamination by byproducts like methane or hydrogen sulfide [29]. Addressing these dynamics is critical for optimizing both storage and in situ production in UHS systems.

Biogeochemical modeling plays a central role in understanding and predicting the complex interactions between microorganisms, geochemical reactions, and fluid dynamics that occur in underground hydrogen storage (UHS). These models provide a critical link between small-scale laboratory observations and large-scale field applications, offering a predictive framework with which to assess storage performance and associated risks across multiple scales [23].

At the small scale, models focus on the microbial metabolism that consumes hydrogen, the dissolution and precipitation of minerals, and the cross-metabolic interactions among different microbial groups [30–32]. Several simulation tools are often employed to simulate the coupling between biological processes and geochemical reactions, providing a detailed understanding of how these processes affect hydrogen storage efficiency and stability [11,12]. Small-scale models, such as pore-scale or 1D–2D models, are particularly valuable for identifying localized effects that influence hydrogen retention [33]. For instance, the dissolution of carbonates (e.g., calcite, dolomite) releases CO_2, which methanogens and acetogens use as a substrate for their metabolism [34]. Similarly, the presence of sulfate minerals (e.g., gypsum, anhydrite) drives sulfate reduction by SRBs, leading to the formation of H_2S, which can be sequestered as pyrite or remain in the gas phase [35,36]. This feedback loop between geochemical reactions and microbial activity is crucial for understanding how the composition of the rock matrix affects microbial behavior [37,38].

As we move to the large scale, reservoir models describe the pressure variations due to hydrogen injection, flow and distribution in porous media, the interaction between hydrogen and remaining hydrocarbons in the reservoir, such as methane, hydrogen diffusion, long-term geochemical changes in the rock and formation water, and the evolution of microbial populations over the storage life [23,26,39]. The transition from a small-scale to a large-scale model poses some significant challenges when it comes to incorporating the localized interactions captured in pore-scale models into the macroscopic fluid flow and heterogeneous properties of the reservoir [40]. In fact, biogeochemical modeling for UHS requires the integration of microbial growth equations, biological reactions, and geochemical processes across different scales.

At the reservoir scale, biogeochemical models extend these insights to capture geological heterogeneity, including variations in lithology and fracture networks [11]. These large-scale models are essential for predicting long-term hydrogen storage behavior under varying operational scenarios. They assess the risks of hydrogen loss or contamination due to microbial byproduct formation (e.g., methane, hydrogen sulfide) and evaluate the effects of geochemical processes on reservoir stability [41]. By integrating data and processes across scales, these models enable a comprehensive evaluation of UHS feasibility, identifying challenges and guiding strategies to optimize storage performance.

One crucial yet often overlooked phenomenon in UHS is biofilm formation. Biofilms are dense microbial communities encased in an extracellular polymeric substance (EPS) that allows them to adhere to solid surfaces and thrive in otherwise harsh subsurface conditions [42]. In the context of UHS, biofilms can have both beneficial and detrimental effects on hydrogen storage; thus, the ability to model biofilm dynamics, in conjunction with microbial metabolisms and geochemical interactions, is critical for predicting the long-term performance of UHS systems [43]. However, modeling biofilms introduces additional challenges, particularly when attempting to scale up from laboratory-based pore-scale models to large-scale reservoir models because laboratory experiments provide valuable insights into localized phenomena, such as biofilm-induced pore clogging or else rock consumption and its effect on hydrogen flow, but do not account for rock heterogeneities and spatial distribution of microbial activity, which can play a significant role at the reservoir scale [44,45].

This paper presents a comprehensive investigation of biogeochemical modeling approaches for UHS, focusing on small-scale models, which capture rock, fluid, and microorganism interactions at the pore scale, and large-scale models, which reproduce reservoir geometry, hydrogen injection at the well(s), induced pressure increase, and fluid dynamics. This paper also explores how to integrate biological, chemical, and physical processes and addresses the challenges of incorporating empirical data collected at the lab scale into the models. The limitations of current tools used to model different scales, reaction kinetics, and reservoir types in simulating the complex feedback mechanisms between microbial and geochemical processes are discussed. Then, this paper offers insights into the future of biogeochemical modeling for UHS, focusing on the need for advanced multiphysics approaches to improve the simulation of the dynamic interplay among biological, chemical, and physical processes in subsurface environments. Eventually, a workflow is suggested that builds on the existing capability of simulating both small-scale and large-scale phenomena to develop accurate UHS models. These models can be used to reliably predict hydrogen storage performance, optimize storage strategies, and assess potential risks associated with hydrogen injection into geological formations.

2. Bacterial Growth Equations and Biological Reactions

Small-scale modeling, particularly at the pore and laboratory scales, is a powerful tool to explore the interactions between microbial activity and geochemical processes. By using modified-Monod kinetics and other mathematical approaches, researchers can simulate microbial growth and reactions under various environmental conditions (e.g., pH, temperature, pressure, electron acceptor availability), capturing the complex interplay between biological and geochemical dynamics and offering key insights into how hydrogen is consumed by microbes, how mineral dissolution and precipitation affect microbial activity, and how cross-metabolic interactions between different microbial groups influence the storage performance.

2.1. Microbial Clusters in UHS Systems and Related Reactions

In UHS, microbial metabolism such as methanogenesis and acetogenesis plays crucial roles in hydrogen consumption. Methanogenic archaea use hydrogen as an electron donor and dissolved carbonate and CO_2 as carbon sources to produce methane. This process is particularly important in anaerobic conditions, typically found in depleted reservoirs or saline aquifers. The availability of CO_2, which can be released from carbonate dissolution or other geochemical processes, is a key driver of methanogenic activity [23,46]. The biochemical reactions for methanogenesis are reported in Table 1. Reactions are highly pH-dependent and require neutral to slightly alkaline conditions to proceed efficiently. Carbonate-rich environments provide a buffer to maintain this pH range, enabling sustained methanogenic activity [25,47].

In parallel with methanogens, acetogenic bacteria convert hydrogen and CO_2 into acetic acid (CH_3COOH) or other fatty acid compounds, which can serve as a substrate for other microbial groups like methanogens or sulfate-reducing bacteria (SRBs) to perform cross-metabolism reactions [30,48]. Acetogenesis is more favorable under conditions where sulfate is scarce, as sulfate-reducing bacteria outcompete acetogens when sulfate is abundant. In UHS, the balance between methanogenesis and acetogenesis can shift depending on the availability of electron acceptors (such as CO_2) and environmental conditions like pH and temperature [22,49].

In sulfate-rich reservoirs, sulfate-reducing bacteria (SRBs) outcompete methanogens and acetogens for hydrogen, using sulfate as an electron acceptor to produce hydrogen sulfide (H_2S). This process not only consumes hydrogen but also leads to the accumulation of toxic H_2S, which poses health hazards for operators and challenges such as well corrosion [43,50]. The kinetics of sulfate reduction are sensitive to the concentrations of sulfate and hydrogen, and SRBs thrive in environments where both are available in abundance. Saline aquifers and depleted gas reservoirs with sulfate minerals (e.g., gypsum and anhydrite) provide electron acceptors, promoting sulfate-reducing activity [51–53].

Iron-reducing bacteria (FeRBs) are another important group in iron-rich formations, which use hydrogen to reduce ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}). Iron reduction affects the redox balance of the storage environment and can lead to mineral transformations, such as the precipitation of siderite ($FeCO_3$) or pyrite (FeS_2) in the presence of H_2S [54,55].

Furthermore, microbial communities in UHS systems do not operate in isolation; they engage in cross-metabolic interactions, where the byproducts of one group serve as substrates for another. For instance, methanogens and acetogens compete for hydrogen, but the acetate produced by acetogens can serve as a substrate for methanogens, and sulfate-reducing bacteria outcompete both methanogens and acetogens when sulfate is available, driving the system towards H_2S production rather than methane or acetate [30,32].

Then, the success of microbial metabolism in UHS systems also depends on the geochemical composition of the reservoir. Rock minerals (e.g., carbonates, sulfates, and iron oxides) provide essential electron acceptors or buffer pH, while the composition of formation water affects microbial growth rates and reaction kinetics [17,23,24]. Carbonate minerals (e.g., calcite, dolomite) dissolve in response to acidic conditions, releasing CO_2, which can be used by methanogens and acetogens [56]. Sulfate minerals (e.g., gypsum, anhydrite) release sulfate ions into the formation water, promoting sulfate reduction. Iron oxides (e.g., hematite, goethite) provide a source of ferric iron for iron-reducing bacteria, which affects the redox potential of the reservoir [10,12,15].

The biogeochemical reactions in UHS differ significantly between saline aquifers and depleted oil or gas reservoirs due to variations in geochemical compositions and microbial ecosystems [57]. In saline aquifers, hydrogen can react with minerals and dissolved compounds such as iron oxides, carbonates, and sulfates, leading to changes in porosity and permeability that influence storage capacity [58]. In contrast, depleted reservoirs, which contain residual hydrocarbons and sulfur compounds, exhibit additional reactions like hydrogenation of hydrocarbons and interactions with sulfur species, often resulting in the formation of hydrogen sulfide (H_2S). These reactions can compromise hydrogen purity and pose safety risks [59]. Microbial activity also varies markedly between the types of reservoirs. In saline aquifers, microbial communities are typically dominated by sulfate-reducing bacteria (SRB), iron-reducing bacteria (IRB), and halophilic methanogens. These microorganisms drive processes such as sulfate reduction and methane production. In depleted reservoirs, the presence of residual hydrocarbons supports a more diverse microbial population, including methanogens and hydrocarbon-degrading bacteria [25]. These organisms can influence hydrogen quality through methane generation and biofilm formation. Understanding these differences is crucial for tailoring UHS strategies to optimize storage efficiency and mitigate risks associated with microbial activity and geochemical reactions.

The main biochemical and cross-metabolism reactions are reported in Table 1. PHREEQC, Comsol, CMG_GEM, DuMuX, and other geochemical modeling tools are commonly used to couple these geochemical reactions with microbial kinetics and account for cross-metabolic interactions, allowing researchers to simulate the precipitation and dissolution of minerals, pH changes, and the availability of electron acceptors in the formation.

Table 1. Main biochemical and cross-metabolism reactions [23,30,32,33,53,60–63].

	Equations
Sulphate-reducing reactions	$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$ $Acetate^- + SO_4^{2-} \rightarrow 2HCO^- + HS^-$ $\mathit{Propionate}^- + 0.75SO_4^{2-} \rightarrow \mathit{Acetate}^- + HCO_3^- + 0.75HS^- + 0.25H^+$ $\mathit{Butyrate}^- + 0.5SO_4^{2-} \rightarrow 2\mathit{Acetate}^- + 0.5HS^- + 0.5H^+$ $\mathit{Lactate}^- + 0.5SO_4^{2-} \rightarrow \mathit{Acetate}^- + HCO_3^- + 0.5HS^-$
Acetogenic reactions	$2CO_2 + 4H_2 \rightarrow \mathit{Acetate} + 2H_2O$ $Glucose \rightarrow 3\mathit{Acetate}^- + 3H^+$ $\mathit{Propionate}^- + 3H_2O \rightarrow \mathit{Acetate}^- + HCO_3^- + H^+ + 3H_2$ $\mathit{Butyrate}^- + 2H_2O \rightarrow 2\mathit{Acetate}^- + H^+ + 2H_2$ $4H_2 + 2HCO_3^- + H^+ \rightarrow \mathit{Acetate}^- + 4H_2O$ $\mathit{Lactate}^- \rightarrow 1.5\mathit{Acetate}^- + 0.5H^+$ $2Acetate + 2HCO_3^- + 10H^+ + 8e^- \rightarrow 2Lactate + 4H_2O$ $2Acetate + 10H^+ + 8e^- \rightarrow 2Ethanol + 2H_2O$
Methanogenic reactions	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ $\mathit{Acetate}^- + H_2O \rightarrow CH_4 + HCO_3^-$ $4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$
Iron-reducing reactions	$2FeOOH + H_2 + 4H^+ \rightarrow 2Fe^{2+} + 4H_2O$ $H_2 + 3Fe^{III}{}_2O_3 \rightarrow 2Fe^{II}{}_3O_4 + H_2O$

The following Table 2 provides a comparative overview of various software tools used for coupled geochemical and biological modeling in UHS scenarios. The tools listed in the table offer various capabilities for simulating coupled geochemical and biological processes at different scales. For each software, the table indicates whether it supports fluid dynamics, geochemical, or biological modeling. Additionally, the table details the scales of modeling (pore-scale, core-scale, reservoir-scale), key limitations, and the main input parameters necessary for implementing UHS models. All information is derived from the studies cited in the tables in Sections 3 and 4.

Table 2. List of software tools for coupled geochemical and biological modeling in underground hydrogen storage (UHS).

Software	Fluid Dynamics	Geochemistry	Biological Processes	Modeling Scales	Key Limitations	Key Input Parameters	Additional Notes
PHREEQC		✓	✓	Core-scale (1D)	*Limitations*: Static equilibrium only; no direct support for fluid modeling. *Strengths*: Robust geochemical modeling, user-friendly interface, extensive reaction databases.	Initial composition of phases, dissolution/precipitation/ reaction kinetics, P-T conditions.	Best suited for equilibrium geochemical simulations; limited dynamic and biological modeling capabilities.
DuMux	✓	✓	✓	Pore-, Core-, Reservoir-scale (1D, 2D, 3D)	*Limitations*: High computational complexity; steep learning curve. *Strengths*: Open-source, supports advanced coupled processes, excellent scalability from pore to reservoir scale.	Rock properties (porosity, permeability), biological and geochemical kinetics, coupled reaction networks.	Open-source and versatile; supports multiphase flow, geochemical, and biological interactions.
MRST	✓	✓	✓	Core-, Reservoir-scale (2D, 3D)	*Limitations*: It requires expertise and computational resources. *Strengths*: Easy-to-use framework for core and reservoir simulations; adaptable to various geometries.	Reservoir geometry, equations of state (EOS), biological and geochemical parameters.	Flexible for reactive transport.
TOUGHREACT	✓	✓	✓	Core-, Reservoir-scale (1D, 2D, 3D)	*Limitations*: Limited support for customizing specific biological reactions. *Strengths*: Proven versatility for multiphase flow and reactive transport; broad range of applications in geochemistry.	Hydrogeological data, mineral reactions, fluid properties.	Versatile for multiphase reactive transport; requires enhancement for specific biogeochemical modeling.
COMSOL Multiphysics	✓	✓	✓	Pore-, Core-, Reservoir-scale (1D, 2D, 3D)	*Limitations*: Requires significant expertise to set up and solve coupled problems. *Strengths*: Highly customizable for complex multiphysics problems; broad range of applications in UHS.	Multiphysics coupling settings, geometry mesh, transport and reaction parameters.	Highly flexible; supports custom coupling of geochemistry, biology, and fluid dynamics.
OpenFOAM	✓	✓	✓	Pore-, Core-, Reservoir-scale (2D, 3D)	*Limitations*: Requires advanced programming skills for customization; computationally demanding. *Strengths*: Open-source flexibility for tailored simulations; robust for reactive transport.	Fluid dynamics properties, reactive transport models, biological and geochemical kinetics.	Open-source; customizable for pore-scale simulations, though computationally demanding.

Table 2. *Cont.*

Software	Fluid Dynamics	Geochemistry	Biological Processes	Modeling Scales	Key Limitations	Key Input Parameters	Additional Notes
ANSYS Fluent	✓	✓		Pore-, Core-, Reservoir-scale (2D, 3D)	*Limitations*: Limited support for biological processes. *Strengths*: Excellent for complex fluid flow simulations; strong geochemical modeling capabilities.	Multiphase flow parameters, geochemical interaction data.	Strong in fluid dynamics and geochemistry; lacks integrated biological modeling capabilities.
Eclipse	✓			Reservoir-scale (3D)	*Limitations*: Limited flexibility for biogeochemical coupling. *Strengths*: Industry-standard for reservoir simulations; reliable for large-scale modeling.	Physical properties of fluids and rocks, initial conditions.	Primarily used for fluid-dynamics reservoir simulations.

2.2. Modeling Approaches for Microbial Growth

Modeling bacterial growth is a crucial element in understanding the biogeochemical dynamics of UHS, as microbial activity significantly affects hydrogen consumption and gas composition. The four key microbial clusters involved—methanogens, sulfate-reducers, iron-reducers, and acetogens—have distinct metabolic pathways that are influenced by environmental conditions such as substrate availability, temperature, and pressure. The growth and activity of these microorganisms are typically modeled using variations on the Monod equation, which describes the specific growth rate as a function of substrate concentration [53,64]. The classical Monod model assumes that the growth rate of microorganisms is proportional to the concentration of a limiting substrate, such as hydrogen, and follows a saturation curve [33,49].

However, to model the complex microbial communities involved in UHS, modified versions of the Monod equation are often employed (Table 3). These models take into account substrate inhibition, competition for nutrients, and the presence of multiple substrates, such as hydrogen and electron acceptors like sulfate or carbon dioxide. Sulfate-reducing bacteria (SRB) and iron-reducers often compete with methanogens for hydrogen, and their growth rates can be suppressed when hydrogen concentrations are low. For instance, the microbial population dynamics model described by Hagemann et al. (2016) integrates the Monod growth function with reactive transport equations to simulate the competition among methanogens, sulfate reducers, and iron reducers [49]. In addition to the Monod model, more advanced approaches, such as the Moser and Haldane equations, introduce modifications to account for inhibitory effects or deviations from ideal conditions [65]. These models incorporate additional parameters, such as an inhibition constant, to reflect the negative impact of high substrate concentrations on microbial growth [48,49]. Table 3 summarizes the most used growth kinetics equations for the key forms of microbial metabolism involved in UHS. However, numerous additional models exist in the literature, such as the Blackman, Aiba-Edwards, Han and Levenspiel, Powell, and other models [65,66]. These models offer alternative approaches for simulating growth dynamics under varying substrate conditions, substrate inhibition levels, and biomass concentrations. Researchers looking to model bacterial growth can refer to the extensive literature to identify the most appropriate empirical model.

Table 3. Growth kinetics equations for microbial metabolisms [33,48,49,64–68].

Model Type	Equation	Characteristics
Classical Monod	$\mu(S) = \mu_{max} \frac{S}{K_S+S}$	It describes the growth rate depending on the substrate concentration, applicable for simple substrate-limited growth without inhibition.
Moser Equation	$\mu(S) = \mu_{max} \frac{S^\eta}{K_S+S^\eta}$	It introduces an additional exponent η to the substrate concentration, offering flexibility for fitting to various microbial growth scenarios.
Panfilov Model	$\mu(S) = \frac{1}{t_n} \frac{n}{1+\left(\frac{n}{n_{max}}\right)^2} \frac{S}{K_S+S}$	It integrates population dynamics with a maximum population size and characteristic eating time; suitable for microbial competition in UHS systems.
Double Monod Model	$\mu(S) = \mu_{max} \frac{S_1}{K_{S1}+S_1} \frac{S_2}{K_{S2}+S_2}$	It accounts for two limiting substrates, such as hydrogen and sulfate, commonly used for environments involving multiple substrate limitations.
Haldane Model	$\mu(S) = \mu_{max} \frac{S}{K_S+S+\frac{S^2}{K_i}}$	This version of the substrate-inhibited Monod model is especially useful when higher substrate concentrations inhibit microbial growth.
Teissier Model	$\mu(S) = \mu_{max}\left(1 - e^{-\frac{S}{k_T}}\right)$	It describes the growth rate as an exponential function, suitable for intermediate substrate concentrations.
Contois Model	$\mu(S) = \mu_{max} \frac{S}{K_S \cdot X+S}$	It incorporates the biomass concentration into the equation, making it useful for high-density cultures with a significant biomass influence on growth kinetics.

3. Small-Scale Biogeochemical Modeling

Small-scale models typically focus on pore-scale and laboratory-scale systems and delve into the interactions between microbial activity, hydrogen consumption, and subsequent biochemical reactions that can both enhance or hinder hydrogen storage. Experimental, numerical, and theoretical studies targeting processes occurring at 1D and 2D scales, in controlled laboratory environments or through simulations representing fine-scale reservoir features, are available in the literature. These models provide crucial insights into the fine-scale interactions among microbial communities, geochemical reactions, and hydrogen flow. Table 4 provides a comprehensive review of recent research in the field of biogeochemical and fluid dynamics modeling applied to UHS. The table collates crucial details from various studies, presenting a comparative overview that emphasizes the methodologies employed, the modeling scales and applied approaches, storage domains, phenomena studied, modeled metabolisms, operating conditions, and key observations.

There are several advantages to using small-scale biogeochemical models, the main ones of which are as follows:

- *Detailed insights into microbial dynamics*: these models allow researchers to simulate microbial growth (see models summarized in Table 3), metabolic rates, and their interactions with the geochemical environment with high precision.
- *Focus on geochemical reactions*: the detailed simulation of geochemical processes, such as mineral dissolution and precipitation, allows for a deeper understanding of how hydrogen interacts with reservoir minerals, influencing porosity and permeability.
- *Validation through laboratory experiments*: models are often validated against experimental data from laboratory tests, ensuring a high accuracy in the simulation of specific processes, such as biofilm formation or microbial hydrogen consumption.
- *Refinement of reaction kinetics*: these models provide an opportunity to calibrate reaction kinetics, such as microbial hydrogen consumption rates, which can then be used to inform larger-scale models.
- *Coupling of biological and geochemical reactions*: closer coupling of microbial kinetics with geochemical reactions, providing insights into feedback loops that occur at the micro-level.

Table 4. Overview of small-scale biogeochemical modeling approaches for UHS.

Title	Authors (Year)	Storage Domain and Modeling Scale	Approach	Phenomena Studied	Modeled Metabolisms	Operating Conditions	Observations	Ref.
Interplay between microbial activity and geochemical reactions during underground hydrogen storage in a seawater-rich formation	A. Shojaee et al. (2024)	Seawater-rich porous media—1D, batch model	Biogeochemical modeling with PHREEQC	Microbial reactions and geochemical reactions	Methanogenesis, acetogenesis, sulfate reduction	Pressure: 300 atm, temperature: 60 °C	Dolomite dissolution buffers pH and maintains microbial activity. H2 loss was greatest in dolomite systems, with complete H2 loss observed in dolomite-rich formations.	[23]
Role of geochemical reactions on caprock integrity during underground hydrogen storage	L. Zeng et al. (2023)	Caprock in depleted gas reservoirs—1D, small-scale	Kinetic batch modeling using PHREEQC	Mineral dissolution/precipitation, H2 diffusion, caprock integrity	Not applicable	Pressure: 16.9 MPa, temperature: 72.2 °C, 30-year simulation	Geochemical reactions show <1% mineral dissolution over 30 years, with caprock integrity maintained with minimal hydrogen diffusion.	[69]
Bioreaction coupled flow simulations: Impacts of methanogenesis on seasonal underground hydrogen storage	G. Wang et al. (2024)	Depleted gas reservoirs—1D, 2D	Bioreaction-coupled hydrodynamic modeling using CMG/GEM and Petrel	Methanogenesis, flow dynamics, hydrogen purity, water-to-gas ratio	Methanogenesis	Pressure: up to 300 atm, time period: 330 days	Methanogenesis degrades hydrogen purity and increases water breakthrough. Scaling theory is validated for larger systems with biogeochemical coupling.	[70]
Numerical simulation of underground hydrogen storage converted from a depleted low-permeability oil reservoir	J. Wang et al. (2024)	Low-permeability oil reservoir—1D, 2D pore scale	Numerical simulation with custom three-dimensional, three-phase mathematical model	Hydrogen seepage, fluid dynamics, interaction with oil and water films	Not applicable	Various injection speeds, heterogeneous rock properties	Hydrogen seepage is hindered by oil films, and reservoir heterogeneity significantly affects injection and production efficiency. Simulations show that up to 25% of hydrogen can be lost to the reservoir due to these effects.	[71]
Phenomenal study of microbial impact on hydrogen storage in aquifers: A coupled multiphysics modelling	Q. Gao et al. (2024)	Porous aquifers—2D	Coupled hydrological–mechanical–chemical–biological multiphysics modeling using COMSOL	Microbial clogging, hydrogen consumption, mineral dissolution/precipitation	Iron-reducing bacteria (IRB)	Injection pressure: 18 MPa, temperature: 47 °C	Microbial activities degrade hydrogen recovery efficiency through clogging and hydrogen consumption. Microbial clogging has the most significant impact on UHS.	[55]
Pore-scale modelling on hydrogen transport in porous media: Implications for hydrogen storage in saline aquifers	J. Wang et al. (2023)	Saline aquifers—3D pore scale	Numerical simulation using the Volume of Fluid (VOF) method in OpenFOAM	Hydrogen flow dynamics, capillary trapping, wettability impact	Not applicable	Pressure: up to 25 MPa, temperature: 323 K	Weakly water-wet systems promote larger hydrogen clusters, leading to significant hydrogen loss during extraction; strong capillary trapping effects are observed.	[72]
Gibbs Energy Dynamic Yield Method (GEDYM): Predicting microbial growth yields under energy-limiting conditions	C. M. Smeaton (2018)	Subsurface, microbial environments—1D	Biomass-explicit biogeochemical modeling using PHREEQC	Microbial growth under energy-limited conditions, bioenergetics	Methanogenesis, sulfate reduction, iron reduction	Variable geochemical conditions	GEDYM provides a dynamic method for calculating microbial growth yields by linking Gibbs energy changes in metabolic reactions to environmental conditions.	[73]

Table 4. *Cont.*

Title	Authors (Year)	Storage Domain and Modeling Scale	Approach	Phenomena Studied	Modeled Metabolisms	Operating Conditions	Observations	Ref.
Determination of Microbial Maintenance in Acetogenesis and Methanogenesis by Experimental and Modeling Techniques	Bonk et al. (2019)	Biogas-producing continuous stirred tank reactors—0-D, small-scale	Modeling using ADM1, thermodynamic black box approach (TBA), and dynamic flux balance analysis (dFBA) in MATLAB	Microbial growth rates, maintenance in acetogenesis, and methanogenesis	Acetogenesis, methanogenesis	Temperature: 37 °C, dilution rates: 0.18 and 0.07 days^{-1}, hydraulic retention times: 5.5 and 14 days	The study reveals much lower microbial maintenance rates for acetogenesis and methanogenesis than previously assumed, with significant deviations from standard model predictions.	[64]
Effect of Iron Mineral Transformation on Long-Term Subsurface Hydrogen Storage—Results from Geochemical Modeling	A. Pathak, S. Sharma (2024)	Iron-rich sedimentary reservoirs—1D, small-scale	Geochemical modeling using Geochemist's Workbench	Hydrogen loss, iron mineral transformation (siderite, magnetite), redox interactions	Not applicable	Temperature: 100 °C, 100-year simulation period	The study shows that hydrogen loss is driven by the transformation of iron minerals like siderite and magnetite, and abiotic hydrogen consumption is linked to dissolved Fe^{2+} activities.	[54]
Hydrogen storage in Majiagou carbonate reservoir in China: Geochemical modelling on carbonate dissolution and hydrogen loss	L. Zeng et al. (2022)	Carbonate reservoirs—1D, small-scale	Geochemical modeling using PHREEQC	Calcite and dolomite dissolution, hydrogen loss, methane generation	Not applicable	Pressure: 90 atm, temperature: 120 °C, simulated time up to 500 yrs	The study indicates that up to 81.1% of hydrogen loss over 500 years was due to fluid–carbonate interactions, with calcite dissolution causing integrity issues and methane generation affecting hydrogen purity.	[74]
Investigating the activity of indigenous microbial communities from Italian depleted gas reservoirs and their possible impact on underground hydrogen storage	R. Bellini et al. (2024)	Depleted gas reservoirs—1D, batch model	Batch experiments with biogeochemical modeling using COMSOL	Microbial activity in nutrient-enriched conditions	Methanogenesis, acetogenesis, sulfate reduction	Temperature: 50 °C, pressure: 2 bar, 23 days	Acetogenic and acidogenic bacteria were dominant in all tested reservoirs, while methanogenic activity was observed primarily in conditions with 50% hydrogen in the headspace.	[48]
Computational Fluid Dynamics Modeling of Rock–Liquid–H2 Contact Angles: Implications for Underground Hydrogen Storage	A. Safari et al. (2024)	Depleted gas reservoirs—2D, pore-scale	Computational fluid dynamics (CFD) modeling using COMSOL	Contact angles, wettability, rock–liquid–H2 interactions	Not applicable	Pressure: 10–100 bar, temperature: 20–80 °C	The study shows how mineral properties influence H2 wettability and detachment, which is crucial for understanding H2 mobility and retention in underground hydrogen storage systems.	[75]
Coupled model for microbial growth and phase mass transfer in pressurized batch reactors in the context of underground hydrogen storage	Strobel et al., 2023	Underground hydrogen storage (porous media)—1D, batch reactor experiments	Modeling: Microbial growth and phase mass transfer, mass transfer between gas and water phases. Implemented in Python using odeint	Methanation	Methanogens	Temp: 65 °C and 37 °C; pressure: 600–1100 mBar	The model allows the prediction of microbial growth, methanation, and phase transfer in underground hydrogen storage scenarios.	[76]
Pore scale modeling on microbial hydrogen consumption and mass transfer of multicomponent gas flow in underground hydrogen storage	Song et al. (2024)	Depleted gas reservoirs—2D/3D pore-scale	Simulation using FLUENT to model biofilm growth, microbial reactions, and mass transfer	Hydrogen consumption, biofilm effects on pore structure, permeability reduction, gas components	Methanogenesis	Pressure: 10 MPa, temperature: 298 K, simulation time: 68.3 days for full biofilm development	Biofilm growth leads to pore clogging, which reduces permeability and storage efficiency, with a potential impact on hydrogen purity.	[77]

3.1. Detailed Insight into Microbial Dynamics

Small-scale models, particularly those focused on pore-scale and laboratory-scale phenomena, provide a highly detailed understanding of microbial dynamics in subsurface environments. Pore-scale modeling is extensively used to investigate the fluid flow behavior and the impact of pore geometry on hydrogen trapping and mobility during UHS. Yu et al. (2024) used OpenFOAM to examine how pore geometry affects residual trapping during cyclic hydrogen injection and withdrawal [78]. Small-scale models typically focus on the physics of multiphase flow in porous media, highlighting phenomena such as capillary trapping, wettability alteration, and hydrogen distribution. At the core scale, Malki et al. (2024) provided experimental data on capillary pressure and relative permeability in hydrogen–water systems [62]. Their experiments demonstrated that relative permeability of hydrogen decreased sharply from 1 to 0.2 as water saturation increased to 50%. This reduction in permeability underscores the competitive displacement between hydrogen and water, significantly impacting hydrogen injectivity and recoverability. Lysyy et al. (2022) conducted 2D micromodel experiments to observe real-time hydrogen displacement and trapping mechanisms, emphasizing the influence of pore structure on hydrogen mobility [79]. Wettability and capillary behavior were further studied by Safari et al. (2024), who applied computational fluid dynamics to measure rock–liquid–H_2 contact angles [75]. These studies underline the importance of pore-scale phenomena in understanding hydrogen mobility, retention, and potential leakage in underground reservoirs.

Bellini et al. (2024) investigated microbial dynamics in depleted gas reservoirs, focusing on microbial growth, particularly methanogenesis and sulfate reduction, which can reduce the volume of stored hydrogen while generating secondary gases like methane (CH_4) and hydrogen sulfide (H_2S) [48]. The study incorporated empirical relationships derived from lab-scale experiments, making it a strong example of modeling microbial activity based on real-environment data. Smeaton et al. (2018) explored microbial hydrogen consumption through methanogenesis and sulfate reduction, showing that microbial activity is a major driver of hydrogen loss in porous media [73]. Their work emphasized the pore-scale interactions between microbial communities and available substrates, including sulfate and organic carbon, which significantly influence hydrogen dynamics.

One of the key strengths of small-scale modeling is its ability to capture the pore-scale fluid dynamics of hydrogen flow in porous media. Several studies, such as those by Wang et al. (2023) and Jadhawar and Saeed (2023), utilized numerical simulations to model how hydrogen migrates through complex pore networks [11,72]. These models revealed that pore structure, pore throat size, and wettability are critical factors in determining the retention and mobility of hydrogen. At the pore scale, capillary forces and surface interactions dominate, meaning that small changes in pore structure (such as those caused by biofilm growth) can drastically affect hydrogen flow [43,72]. In particular, the findings of Wang et al. (2023) indicate that in hydrophilic reservoirs, hydrogen tends to be retained more effectively due to higher residual saturation, which was observed to be approximately 20%. Conversely, under hydrophobic conditions, residual hydrogen saturation was reduced to as low as 5%, significantly enhancing hydrogen mobility but reducing its long-term trapping efficiency [72]. Furthermore, studies like that of Veshareh et al. (2022) use theoretical growth rates for microbial activity based on literature-derived values to predict best- and worst-case scenarios in hydrogen storage [33]. Strobel et al. (2023) developed a coupled model for microbial growth and phase mass transfer in pressurized batch reactors, focusing on methanogenesis and using Python to solve differential equations. This approach is particularly useful for studying microbial dynamics and hydrogen consumption in small-scale UHS systems, providing valuable insights into how microorganisms influence phase transfer and hydrogen retention in porous environments [76]. The use of equilibrium and kinetic models in these studies helps researchers forecast how biochemical and geochemical processes evolve over time, guiding the design of effective UHS strategies.

3.2. Pore-Scale Biofilm Formation

Another critical phenomenon observed in the biochemical modeling of UHS is biofilm formation, which can lead to pore clogging and reduced permeability in the reservoir. Liu et al. (2024) studied the impact of biofilm growth on hydrogen flow through porous media. Their microfluidic experiments demonstrated how sulfate-reducing bacteria form biofilms that clog pore spaces, leading to reduced hydrogen mobility and retention [42]. Biofilm-induced clogging is particularly important in storage systems because it directly affects hydrogen flow. The approach taken by Liu et al. (2024) integrates empirical data on biofilm growth, making it highly relevant for predicting long-term reservoir performance in the presence of active microbial communities. The studies by Ali et al. (2023) and Liu et al. (2023) demonstrated how biofilm formation within porous media further exacerbates hydrogen retention challenges [43,80]. Biofilm-forming bacteria not only consume hydrogen but also alter the physical properties of the storage media by changing its wettability, pore structure, and effective permeability to hydrogen, thereby affecting hydrogen flow and trapping [50]. Numerical models using platforms like Comsol and MATLAB were employed to simulate these effects at the pore scale, providing insights into the complex interplay between microbial activity and reservoir conditions, as reported in Table 3.

3.3. Validation Through Laboratory Experiments

Many small-scale models were validated against experimental data, making them highly reliable for understanding specific biochemical processes. Studies like those of Gao et al. (2024) and Bellini et al. (2024) integrate empirical data from laboratory experiments, such as microbial growth rates and biofilm formation, to create accurate models of hydrogen consumption and gas production [48,55]. Gao et al. (2024) further highlighted the role of hydrogen-oxidizing microorganisms, specifically iron-reducing bacteria (IRB), in consuming hydrogen during UHS in aquifers. Their 2D reservoir-scale models demonstrated how microbial clogging and hydrogen consumption can alter flow dynamics and reduce hydrogen availability. This study emphasized the need for coupled multiphysics models that account for microbial transport, biofilm formation, and the subsequent impact on reservoir permeability [55]. This direct link between experiments and models ensures that the predictions made at small scales are grounded in observable reality, which is crucial for developing strategies to mitigate hydrogen loss due to microorganisms in UHS [81].

3.4. Refinement of Biogeochemical Reaction Kinetics

Small-scale models allow for the detailed calibration of reaction kinetics, such as microbial hydrogen consumption rates and gas generation rates (e.g., methane or hydrogen sulfide) [64]. These parameters are also crucial for large-scale simulations but can be difficult to be accurately matched in field-scale models. By refining the reaction rates in small-scale models, researchers can provide more accurate inputs for large-scale reservoir models, improving the overall predictability of UHS systems. Bellini et al. (2024) and Veshareh et al. (2022) modeled key biochemical reactions such as methanogenesis and sulfate reduction. These reactions are driven by microbial activity, which is modeled using kinetic rates derived from experimental studies [33,48,82]. Veshareh et al. (2022) employed 1D simulations with PHREEQC to assess the impact of these biochemical processes on hydrogen storage, highlighting the importance of modeling both worst-case and best-case microbial activity scenarios [33].

3.5. Coupling Biochemical and Geochemical Reactions

The close coupling of biochemical reactions with geochemical processes in small-scale models offers insights into how microbial activity can trigger or influence mineral dissolution, precipitation, and changes in porosity [83]. Studies like those of Zeng et al. (2023) and Bo et al. (2021) demonstrate how microbial hydrogen consumption can lead to significant geochemical changes, such as the dissolution of calcite or other minerals [31,69]. Gao et al. (2024) modeled the impact of microbial hydrogen consumption on mineral dissolution and the resulting changes in reservoir porosity. This type of coupled modeling is critical because it shows how biochemical reactions can lead to larger-scale geochemical alterations that may affect reservoir integrity over time [55]. Zeng et al. (2023) modeled the combined effect of biochemical and geochemical reactions, focusing on the dissolution of minerals like calcite under the influence of hydrogen and microbial activity. Biogeochemical models use reactive transport frameworks to predict how biochemical reactions, such as sulfate reduction, can alter the chemical environment of the reservoir, potentially leading to secondary reactions that compromise storage integrity [57]. The dissolution of minerals like pyrite, gypsum, and calcite not only changes the geochemical composition of the reservoir but also impacts the microbial redox reactions, particularly those involving sulfate-reducing bacteria (SRBs) that produce H_2S as a byproduct [23,55,84]. Studies like the one from Al-Yaseri et al. (2022) further explored the hydrogen–brine–rock interactions in depleted reservoirs and aquifers. They demonstrated how hydrogen reacts with rock minerals, altering porosity and permeability through dissolution and precipitation reactions [35]. These geochemical changes, in turn, affect the availability of hydrogen for microbial consumption. In addition, iron-reducing bacteria (FeRBs) play a significant role in hydrogen consumption, particularly in reservoirs rich in iron oxides. Pathak et al. (2024) demonstrated how the reduction of iron minerals by FeRBs could lead to significant hydrogen loss through abiotic reactions coupled with microbial activity. The reduction of Fe(III) to Fe(II) not only consumes hydrogen but also alters the redox state of the reservoir, further affecting other microbial processes such as methanogenesis [85].

In many of these reported studies, the empirical relations between geochemical and microbial processes were modeled using PHREEQC, which allowed for precise simulations of hydrogen–mineral interactions and microbial growth [15,47,53].

3.6. Challenges and Limitations

Small-scale biochemical modeling provides valuable insights into hydrogen consumption, biofilm formation, mineral dissolution, and the feedback loops between microbial activity and reservoir conditions. However, there are several challenges and limitations when applying these findings to large-scale reservoir models, where larger-scale heterogeneities and long-term dynamics must be considered:

- *Scale-dependence of processes*: The behavior of biochemical reactions observed at the laboratory scale may not always scale linearly to the reservoir scale. For example, microbial growth and biofilm formation, while significant in laboratory experiments, may be less impactful at large scales due to the dilution effect and the heterogeneous distribution of microbial communities in the reservoir. Small-scale models often assume homogeneous conditions that are not representative of the more complex and heterogeneous environments of full-scale reservoirs.
- *Limited representation of reservoir heterogeneity*: Small-scale models tend to oversimplify reservoir heterogeneity, particularly in terms of pore structure, flow paths, and spatial distribution of microbial communities. In real reservoirs, variations in permeability, porosity, and mineral composition can lead to different reaction rates and flow behaviors, which are difficult to capture in small-scale experiments or simulations. Although difficult to describe, large-scale models need to account for these heterogeneities, which can significantly alter the outcome of biochemical reactions.
- *Boundary conditions and scaling effects*: Boundary conditions that are imposed in laboratory and pore-scale models are often idealized and do not fully capture the complexity of natural systems. For instance, the supply of nutrients or hydrogen to microbial communities in a lab setting is often uniform, whereas in a reservoir, the distribution of these resources can be highly variable. This discrepancy can lead to overestimations or underestimations of microbial activity when transitioning from small-scale to large-scale models.
- *Incorporation of field data*: While small-scale models rely heavily on experimental data, large-scale models need to incorporate field data, such as reservoir pressure,

temperature, and flow dynamics, which are often unavailable or difficult to measure in the context of small-scale biochemical modeling. As a result, small-scale models may miss key factors that influence microbial behavior and biochemical reactions at larger scales.

- *Time scales of reactions*: The time scales at which biochemical reactions occur can differ between small-scale and large-scale systems. Microbial growth and biofilm formation may occur quickly in a controlled laboratory environment but can take significantly longer in field conditions where environmental factors such as nutrient availability and competition among microbial species play an important role. This temporal scaling issue makes it challenging to directly apply small-scale results to predict the long-term behavior of UHS systems.

Despite these challenges and limitations, small-scale biochemical modeling remains essential for building foundational knowledge of the processes that govern hydrogen behavior in UHS systems. To bridge the gap between small-scale and reservoir-scale models, researchers must incorporate field data and account for the heterogeneities and scaling effects that arise in real-environment reservoir systems.

4. Coupled Biogeochemical–Fluid Flow Modeling at the Reservoir Scale

An overview of the reservoir-scale biogeochemical modeling approaches reported in the scientific literature is provided in Table 4. Most large-scale models account for the multiphysics nature of UHS, integrating microbial kinetics, gas transport, and geochemical reactions. Many advanced modeling platforms, such as PHREEQC, CMG-GEM, Eclipse, and DuMux, allow for the coupling of these processes within a unified framework, and can describe how microbial activity and mineral–fluid interactions influence hydrogen storage over time. Integrating biological phenomena into these models remains a key challenge due to the complex and dynamic interactions among microbial populations, geochemical changes, and reservoir conditions. As already discussed, biofilm formation by hydrogen-consuming microorganisms can significantly alter the flow characteristics of the reservoir, while microbial-driven mineral precipitation can lead to localized reductions in permeability. As demonstrated by Song et al. (2024) and Shojaee et al. (2023), the inclusion of these processes in large-scale models is crucial for reliably predicting long-term hydrogen storage performance [23,77]. Table 5 synthesizes the pivotal contributions and methodologies employed in reservoir-scale biogeochemical modeling for UHS, showcasing several approaches and insights from recent research. The table offers a strategic compilation of studies, emphasizing the complexity of scaling biogeochemical processes to larger geological settings, which are critical for the effective implementation and optimization of UHS systems.

In the following, an expanded synthesis that incorporates findings from several studies is presented to evaluate how large-scale reservoir models address biological and geochemical phenomena.

4.1. Microbial Hydrogen Consumption and Broader Biogeochemical Pathways

Microbial hydrogen consumption is a central concern in the modeling of UHS. The most extensively studied microbial process in this context is methanogenesis. Methanogens are widely present in subsurface environments, particularly in depleted gas reservoirs and saline aquifers, where they can thrive in anoxic conditions.

Table 5. Overview of reservoir-scale biogeochemical modeling approaches for UHS.

Title	Authors (Year)	Storage and Modeling Domain	Approach	Phenomena Studied	Modeled Metabolisms	Operating Conditions	Observations	Ref.
Assessing and modeling hydrogen reactivity in underground hydrogen storage: A review and models simulating the Lobodice town gas storage	J. Tremosa, et al. (2023)	Sandstone gas reservoir, 1D model	Biogeochemical modeling PHREEQC	Hydrogen consumption, methanogenesis, acetogenesis, sulfate reduction	Methanogenesis, sulfate reduction, acetogenesis	Initial pressure 4–5.9 MPa, temperature 25–45 °C, 7-month storage cycle	Methanogenesis leads to significant hydrogen loss; microbial activity influences reaction rates; calibration is needed for kinetic models	[52]
Large-scale underground hydrogen storage: Integrated modeling of reservoir-wellbore system	M. Abdellatif et al. (2023)	Depleted gas field (Viking A field, North Sea), 3D model	Integrated reservoir-wellbore numerical modeling in CMG-GEM	Cushion gas impact, hydrogen diffusion, injection-production strategy	Not applicable	Initial pressure ~500 psi, temperature 183°F, hydrogen injection/production cycles over 6 years	The choice of cushion gas affects hydrogen purity, with methane performing best; hydrogen diffusion has a marginal effect on performance	[41]
Estimating microbial growth and hydrogen consumption in hydrogen storage in porous media	E. M. Thaysen (2021)	Depleted oil and gas fields (DOGFs)	Microbial modeling in porous media	Microbial hydrogen consumption, methanogenesis, homoacetogenesis, sulfate reduction	Methanogenesis, homoacetogenesis, sulfate reduction	Temperature 22.5–80 °C, salinity 0–5 M NaCl, various pressure conditions	Microbial hydrogen consumption is minimal in most fields; only a small percentage of hydrogen is lost due to microbial processes	[25]
Numerical simulation of large-scale seasonal hydrogen storage in an anticline aquifer	M. Chai et al. (2023)	Anticline aquifer, 3D model	Numerical compositional modeling in CMG-GEM	Hydrogen round-trip efficiency, cushion gas injection, trapping mechanisms	Not applicable	Initial pressure 6400 kPa, temperature 50 °C, multiple cycles of hydrogen injection	Nitrogen as cushion gas improves round-trip efficiency from 50% to 70%; CO_2 leads to hydrogen consumption via methanation reaction	[86]
Efficiency assessment of underground biomethanation with hydrogen and carbon dioxide in depleted gas reservoirs: A biogeochemical simulation	L. Wu, et al. (2023)	Depleted gas reservoirs	Biogeochemical simulation with PHREEQC	Biomethanation efficiency, CO_2 sequestration, hydrogen consumption	Methanogenesis	Pressure 50–90 atm, temperature 40 °C, salinity variation, 360 days of simulated time	Biomethanation efficiency reached 94.2% after 360 days; CO_2 sequestration enhances gas storage; salinity and temperature affect methanogen growth and methane production	[87]
Impact of Pore Clogging by Bacteria on Underground Hydrogen Storage	N. Eddaoui, et al. (2021)	Anticlinal aquifer, 3D model	Numerical two-phase flow modeling in DuMuX	Bio-clogging, gas migration, bacterial attachment/detachment	Methanogenesis	Various gas injection rates, reservoir pressure ~20 MPa, temperature ~25 °C	Bio-clogging reduces vertical hydrogen migration and enhances horizontal gas spreading; pore-clogging helps regulate gas flow	[44]

Table 5. *Cont.*

Title	Authors (Year)	Storage and Modeling Domain	Approach	Phenomena Studied	Modeled Metabolisms	Operating Conditions	Observations	Ref.
Hydrogeochemical Modeling to Identify Potential Risks of Underground Hydrogen Storage in Depleted Gas Fields	C. Hemme, et al. (2018)	Depleted gas fields	Hydrogeochemical modeling with PHREEQC	Hydrogen conversion to CH_4 and H_2S, gas–water–rock interactions, diffusion	Methanogenesis, sulfate reduction	Temperature 40 °C, pressure 40 atm, 30-year storage cycle	Bacterial conversion of hydrogen to CH_4 and H_2S, porosity reduction in reservoir and cap rock, minimal hydrogen loss by diffusion	[53]
Numerical simulation of hydrodynamic and gas mixing processes in underground hydrogen storages	F. Feldmann, et al. (2016)	Depleted gas reservoir	Compositional two-phase flow modeling	Gas mixing, density contrast, viscous fingering, molecular diffusion, mechanical dispersion	Not applicable	Initial pressure 170 bar, hydrogen injection for 5 years, cyclic operation for 5 years	Hydrogen mixing with residual gas, hydrogen purity initially low but improves with successive cycles; risk of viscous fingering and gravity override	[88]
Benchmark study for the simulation of Underground Hydrogen Storage operations	S. Hogeweg, et al. (2022)	Generic sandstone gas reservoir	Reservoir simulation using ECLIPSE and DuMux	Fluid dynamics, gas mixing, microbial activity	Methanogenesis	Pressure 82–100 bar, temperature 60 °C, multi-cycle injection/production schedule	ECLIPSE shows greater user-friendliness, but DuMux offers better customization for biochemical reactions; microbial activity reduces hydrogen purity over time	[89]
Modeling hydrogen-rock-brine interactions for the Jurassic reservoir and cap rocks from Polish Lowlands	K. Labus, et al. (2022)	Jurassic sandstone, mudstone, and claystone formations	Geochemical modeling using Geochemist's Workbench (GWB)	Mineral dissolution/precipitation, porosity changes, cap rock integrity	Not applicable	Pressure <12.5 MPa, temperature <50 °C	Goethite and pyrite reactions reduce hydrogen fugacity and porosity; significant risk of cap rock degradation in claystones, while sandstones show more stability	[47]
Development and calibration of a bio-geo-reactive transport model for UHS	S. Hogeweg, et al. (2024)	Porous media, depleted gas reservoirs	Biogeo-reactive transport modeling using DuMux	Methanogenesis, sulfate reduction, pyrite reduction	Methanogenesis, sulfate reduction	Pressure 80 bar, temperature 80 °C, multi-cycle injection/production schedule of 90 days	The model shows permanent hydrogen losses from microbial and geochemical reactions, with increasing hydrogen sulfide and methane contamination over cycles	[51]
Hydrogen storage in geological porous media: Solubility, mineral trapping, H_2S generation, and salt precipitation	R. Gholami (2023)	Depleted gas reservoirs, saline aquifers	Thermodynamic and kinetic modeling with PHREEQC	Hydrogen solubility, mineral trapping, H_2S generation, salt precipitation	Not applicable	Temperature 50–100 °C, pressure up to 30 MPa	The study demonstrates significant H_2S production due to pyrite reduction and salt precipitation after 10 years of operation. Mineral interactions affect injectivity and storage integrity	[24]

Table 5. *Cont.*

Title	Authors (Year)	Storage and Modeling Domain	Approach	Phenomena Studied	Modeled Metabolisms	Operating Conditions	Observations	Ref.
Developing a numerical model for microbial methanation in a depleted hydrocarbon reservoir	Z. Safari et al. (2024)	Depleted hydrocarbon reservoirs	Numerical simulation using MATLAB Reservoir Simulation Toolbox (MRST)	Methanation, CO_2 and H_2 injection, microbial population dynamics	Methanogenesis	Pressure: 40 bar, temperature: 60 °C, 12-year simulation	The model demonstrates how methanogenic bacteria convert injected CO_2 and H_2 into methane, with the microbial population being the most critical factor for methane purity and production	[90]
Geochemical Effects on Storage Gases and Reservoir Rock during Underground Hydrogen Storage: A Depleted North Sea Oil Reservoir Case Study	M. Saeed et al. (2023)	Depleted North Sea oil reservoir	Geochemical modeling using PHREEQC	Mineral dissolution, gas loss, cushion gas effects	Not applicable	Pressure up to 400 atm, temperature: 100 °C	Hydrogen loss over 30 years was negligible (2%), but CO_2 loss was significant (up to 72%). Reservoir porosity and permeability increased due to mineral dissolution	[91]
Application of Analytical Solutions of the Reactive Transport Equation for Underground Methanation Reactors	Hagemann et al. (2024)	Depleted gas reservoirs, 1D and 3D	Analytical solutions compared with DuMux	Methane production, gas transport, bioreactive flow	Methanogenesis	Pressure: 118 bar, temperature: 40 °C, simulation time: up to 500 days	Analytical models offer fast estimates but neglect factors like microbial growth dynamics and two-phase flow; numerical models capture more complex reservoir behavior	[92]

Wu et al. (2023) utilized PHREEQC to simulate biogeochemical reactions in depleted gas reservoirs, focusing on biomethanation [87]. Their findings showed that methanogenesis can play a dominant role in reducing hydrogen storage efficiency, particularly in reservoirs rich in carbon dioxide. Safari et al. (2024) developed a numerical model to simulate microbial methanation in depleted hydrocarbon reservoirs, demonstrating how microbial populations convert injected CO2 and hydrogen into methane. Their model highlights the importance of microbial population dynamics in determining methane purity and production [90]. The simulations results of Safari et al. (2024) demonstrated that microbial activity could convert up to 96% of injected hydrogen and CO_2 into methane over a 12-year period, under optimal conditions with high microbial concentrations (1×10^7 microorganisms/m^3) and sufficient reactants. These results closely align with experimental observations, which showed similar trends in methane purity and microbial growth under comparable temperature and pressure conditions. The study also highlighted the sensitivity of methane production to reservoir parameters: higher initial pressures improved methane yield due to increased reactant availability in the liquid phase, while elevated temperatures suppressed microbial activity, reducing methane output. While methane generation could enhance the reservoir's energy storage potential, it reduces hydrogen purity, posing challenges for its retrieval. Additionally, microbial activity and water production from methanation reactions could potentially impact hydrogen injectivity and recovery efficiency. Similarly, Hogeweg et al. (2022) implemented a coupled hydrodynamic and microbial model using DuMux, focusing on fluid dynamics, microbial growth, decay, and the impact of methanogenesis on UHS. They demonstrated that methanogenesis significantly reduces hydrogen storage capacity over long-term operations [89].

Other microbial pathways, such as acetogenesis, are also active in UHS environments. Acetogens convert hydrogen and carbon dioxide into acetate and other VFAs, which are further consumed by other microbial populations. While less investigated than methanogenesis, these processes too consume hydrogen and contribute to storage inefficiencies [64]. Acetogenesis tends to occur under conditions where methanogens are not dominant, such as in environments with little availability of carbon dioxide or with specific nutrient limitations [47]. Shojaee et al. (2024) explored the dynamics of acetogenesis alongside methanogenesis in a seawater-rich formation [23]. Their model revealed that even if methanogenesis was the dominant pathway for hydrogen consumption, acetogenesis also played a substantial role, particularly in regions of the reservoir with lower carbon dioxide concentrations. The study highlighted how acetogenesis can act as an additional hydrogen sink, further reducing the overall efficiency of UHS. Furthermore, the results of Shojaee et al. (2024) showed that hydrogen concentrations decreased by 35% over a 30-day period due to microbial consumption, accompanied by the production of methane at concentrations reaching 15 mmol/L. These findings illustrate the potential for significant hydrogen loss in microbial-active reservoirs, emphasizing the need for effective microbial control strategies. Similarly, Hemme et al. (2018) modeled hydrogen-to-methane conversion during core-scale experiments and observed methane generation rates peaking at 0.25 mmol/day [53]. Over the duration of the experiment, this process corresponded to a 20% reduction in available hydrogen, highlighting the critical need to account for biogeochemical reactions in reservoir design and management.

Sulfate-reducing bacteria and iron-reducing bacteria add further complexity by generating secondary gases (H_2S in the case of sulfate reduction) and altering the geochemical composition of the reservoir rock through mineral reduction [48,55]. In anoxic environments where sulfate is available, SRBs can outcompete methanogens and acetogens for hydrogen. In turn, of H_2S can also react with minerals, potentially altering reservoir porosity and permeability [47]. For instance, Labus and Tarkowski (2022) showed how hydrogen-induced sulfate reduction led to the formation of hydrogen sulfide in a saline aquifer [47]. Their model predicted that sulfate-reducing bacteria would be highly active in regions of the reservoir where sulfate was abundant, leading to considerable hydrogen consumption. Additionally, the presence of H_2S increased the geochemical complexity of the system by reacting with reservoir minerals, affecting caprock integrity and reservoir permeability [69].

Iron-reducing bacteria (IRBs) represent yet another metabolic pathway for hydrogen consumption in subsurface environments. Iron reduction involves the reduction of ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}) using hydrogen as an electron donor. Although less commonly studied than methanogenesis and sulfate reduction, iron reduction can play a significant role in hydrogen loss, especially in reservoirs rich in iron-bearing minerals like goethite and hematite [52].

In summary, all the studies concur in showing how methanogens, acetogens, sulfate-reducing bacteria, and iron-reducing bacteria consume hydrogen in different ways, with varying implications for reservoir dynamics. This diversity of microbial metabolisms in subsurface environments complicates the efforts to model and predict the long-term behavior of UHS systems. Furthermore, the presence of multiple metabolic pathways operating concurrently in a reservoir can lead to highly heterogeneous hydrogen consumption patterns, which are difficult to capture, and significant challenges remain when it comes to predicting the spatial and temporal distribution of microbial activity in reservoirs.

4.2. Biofilm Formation and Its Impact on Permeability

In the context of UHS, hydrogen-consuming microorganisms can form biofilms within the reservoir rocks [42]. Biofilms tend to grow in response to nutrient availability, including hydrogen. As the biofilm mass increases, it can block pore spaces, thus restricting the flow of hydrogen within the reservoir [44]. This phenomenon is especially relevant in heterogeneous reservoirs, where different regions may experience varying levels of biofilm growth. Studies have shown that biofilm accumulation can be spatially uneven, leading to localized areas of reduced permeability, which create flow heterogeneities and gas trapping zones, reducing the mobility of the gas and increasing the difficulty of withdrawing hydrogen [50].

Song et al. (2024) conducted a detailed pore-scale study using FLUENT, a computational fluid dynamics tool, to simulate the effects of biofilm formation on gas transport in depleted gas reservoirs [77]. Their model integrated microbial hydrogen consumption with multicomponent gas flow dynamics, revealing how biofilm growth decreases porosity and permeability in the affected regions. The study demonstrated that biofilms not only slow gas flow but also create flow heterogeneities, with some areas experiencing near-total blockage of gas pathways, while others remain more permeable [77]. As hydrogen flow becomes restricted in biofilm-affected areas, pressure builds up, potentially leading to preferential flow paths. The findings of Song et al. (2024) also underscore the pivotal role of the initial microbial conditions and pore structure in determining storage efficiency. For instance, increasing the initial microbial saturation volume fraction from 1×10^{-5} to 0.1 resulted in a substantial reduction in the biofilm-water layer growth time, from 90 days to 38.3 days, thereby markedly affecting permeability and porosity. Their simulations showed that under nutrient-rich conditions, biofilm development could decrease permeability by up to 40%, particularly in finer-grained sediments with smaller pore throats. This reduction in permeability directly impacts the injectivity of hydrogen and the effective utilization of pore space, leading to an estimated decrease of 15–25% in the overall storage capacity. Additionally, the study demonstrated that optimizing the biomass decay coefficient could effectively mitigate hydrogen loss and preserve storage efficiency by reducing excessive biofilm growth under specific conditions. Eddaoui et al. (2021) developed a comprehensive two-phase flow model using DuMuX to simulate the effects of bio-clogging on hydrogen migration in anticlinal aquifers [44]. Their model incorporated bacterial attachment, detachment, and pore-clogging processes, showing how microbial activity reduces vertical hydrogen migration while promoting more uniform horizontal spreading. The study revealed that bio-clogging not only impedes vertical gas flow but also enhances gas retention and distribution by creating low-permeability zones around the injection well. In long-term UHS operations, biofilm formation can lead to permanent alterations of the reservoir properties, making it increasingly difficult to inject and withdraw hydrogen effectively.

As biofilms accumulate over time, they not only reduce permeability but can also contribute to the precipitation of minerals within the reservoir, which further clog pore spaces. This biofilm–mineral interaction is particularly relevant in UHS systems that rely on multicycle operations, where hydrogen is repeatedly injected and withdrawn from the reservoir. The spatial heterogeneity introduced by biofilms underlines the need to consider localized biofilm growth and its effects on porosity and permeability in reservoir models [77,93].

4.3. Coupling of Geochemical and Biochemical Reactions

Reservoir models that only account for fluid flow and microbial consumption are insufficient, as they do not capture the dynamic interactions between biological processes and geochemical reactions [70]. For instance, the precipitation of secondary minerals and the dissolution of reservoir rocks must be integrated into large-scale models to predict long-term performance accurately.

Labus and Tarkowski (2022) emphasized the importance of integrating coupled processes into UHS models. Their study showed how the biogeochemical environment within a hydrogen storage reservoir is highly dynamic, with microbial consumption of hydrogen driving changes in mineral composition and fluid flow. One notable example is a saline aquifer where microbial hydrogen consumption led to the formation of H_2S, which subsequently reacted with minerals like pyrite or gypsum, altering the reservoir's geochemical environment [47]. The study showed that microbial hydrogen consumption can destabilize mineral phases, resulting in porosity changes and affecting caprock integrity. Furthermore, they investigated how microbial hydrogen consumption induced the precipitation of secondary minerals like goethite ($FeO(OH)$) and siderite ($FeCO_3$) in a depleted gas reservoir. The study also showed that the spatial distribution of mineral precipitation was uneven, leading to localized reductions in permeability, which further complicated fluid flow and gas extraction.

Additionally, methanogenesis can impact mineral stability, particularly through the production of methane in carbonate-rich formations. Heinemann et al. (2021) demonstrated that the interaction between methane and carbonate minerals leads to carbonate dissolution [26]. Moreover, the dissolution of carbonates during methanogenesis can further destabilize the reservoir structure, leading to increased permeability in certain areas, which can enhance gas mobility but also risk uncontrolled gas migration. Hemme and van Berk (2018) discuss how hydrogeochemical modeling with PHREEQC identifies the risks associated with microbial hydrogen conversion into methane (CH_4) and hydrogen sulfide (H_2S), and its implications for reservoir stability, showing that these processes can significantly affect porosity and hydrogen retention in depleted gas fields [53]. Shojaee et al. (2023) found that carbonate dissolution, coupled with methane production, led to increased fluid mobility, but it could induce the risk of gas leaking [23].

In cases where sulfate-reducing bacteria produce H_2S, the resulting reaction with minerals like pyrite leads to the dissolution of the mineral matrix [24]. These processes were reproduced by Labus and Tarkowski (2022), who modeled the impact of sulfate reduction on pyrite dissolution, claiming that significant hydrogen loss could occur due to the formation of fractures [47].

Beyond microbial activity, mineral–fluid interactions further complicate the storage of hydrogen. Hydrogen is highly reactive and engages in numerous geochemical reactions with the surrounding minerals and fluids, particularly in saline aquifers and gas reservoirs where the chemical composition of the formation water and minerals can vary significantly [24]. These reactions can affect the solubility and mobility of hydrogen [87,94]. Studies by Abdellatif et al. (2023) and Feldmann et al. (2016) have explored how hydrogen mixes with other gases in the reservoir, revealing the challenges of maintaining high hydrogen purity during extraction [41,88]. Feldmann et al. (2016) conducted a comprehensive numerical study to evaluate the hydrodynamic and gas mixing processes during UHS operations [88]. The simulations revealed diffusion rates ranging from 0.1 to 0.5 m/day, influenced by variations in pressure and temperature. Laboratory experiments corroborated these findings, demonstrating similar gas migration patterns within porous media. The study also highlighted that excessive diffusion could lead to undesired gas migration, potentially reducing localized hydrogen storage efficiency by up to 15%. The correlation between the numerical simulations and experimental results underscores the reliability of the model, particularly for predicting gas mixing behavior under varying operational conditions. These insights are critical for optimizing injection pressures and designing storage protocols to enhance UHS performance and safety. The study emphasizes the importance of understanding the interplay between hydrodynamic factors and gas mixing dynamics, providing a framework for mitigating diffusion-related inefficiencies in UHS applications.

4.4. Multiphysics Approaches to Hydrogen Storage Modeling

Given the inherent complexity of biogeochemical processes in UHS systems, multiphysics modeling approaches are necessary to capture the full range of interactions between fluid dynamics, microbial activity, and geochemical reactions. These models integrate multiple physical processes within a single framework, allowing for the simulation of the interaction of different phenomena, such as microbial hydrogen consumption, gas-phase mixing, and mineral reactions, over time and space in a reservoir. Traditional models often treat these processes in isolation, leading to oversimplifications in the predictions of hydrogen storage performance [11,34]. Conversely, multiphysics models incorporate microbial kinetics, gas transport, and chemical reactions simultaneously, providing a comprehensive view of how these processes can influence hydrogen storage efficiency.

Abdellatif et al. (2023) used CMG-GEM to simulate hydrogen storage in a large-scale model, incorporating gas-phase mixing and fluid flow dynamics [41]. In particular, at the field scale, Abdellatif et al. (2023) employed numerical simulations to study hydrogen injection and recovery dynamics in a depleted gas reservoir. Over five injection–recovery cycles, hydrogen saturation was observed to decrease from 0.95 to 0.85 due to gas–gas mixing and minor geochemical reactions. High-pressure laboratory studies supported these findings, showing retention losses of approximately 8–10% under similar conditions. These results suggest that while retention losses remain relatively minor, they could accumulate over successive operational cycles, reducing long-term storage efficiency. The field-scale simulations also highlighted the role of pressure management, as minor adjustments in injection pressure (±5%) could mitigate mixing losses and improve hydrogen retention. Hogeweg et al. (2022) conducted a benchmark study comparing ECLIPSE and DuMux for simulating UHS operations. While ECLIPSE offers a more user-friendly interface, DuMux allows greater customization for biochemical reactions, making it particularly suited for modeling microbial processes like methanogenesis, which affects hydrogen purity over long-term storage [89].

Similarly, Wu et al. (2023) and Hogeweg et al. (2024) employed a reactive transport model to explore how microbial hydrogen consumption interacts with mineral dissolution and precipitation in a reservoir converted into hydrogen storage [51,87]. Their multiphysics approach showed that mineral reactions could have a significant impact on porosity and permeability, with secondary mineral formation blocking pore spaces and reducing fluid mobility. The integration of geochemical reactions with microbial activity allowed the model to reproduce the non-linear feedback loops that arise when biological and geochemical processes interact. As hydrogen could be stored in a mixture with natural gas, typically containing methane but also small quantities of carbon dioxide or nitrogen, the interaction between these gases should also be considered [95]. The simulations of Hogeweg et al. (2024) reported permanent hydrogen losses of up to 10%, primarily due to microbial methanogenesis and sulfate reduction [51]. These results align closely with laboratory findings, where microbial consumption accounted for hydrogen losses ranging between

8% and 12% under controlled experimental conditions. Additionally, field-scale models revealed that heterogeneities in reservoir properties could exacerbate hydrogen losses, with regions of lower microbial activity retaining up to 15% more hydrogen compared to regions with high microbial activity. Capillary forces and gas-phase mixing are critical phenomena that influence how hydrogen moves within the reservoir and how easily it can be recovered. Feldmann et al. (2016) explored these issues in a multiphase flow model that incorporated capillary effects in a porous reservoir [88]. Their findings revealed that capillary forces can lead to localized trapping of hydrogen. In heterogeneous reservoirs, these capillary effects are even more pronounced, as gas-phase interactions and microbial consumption create complex flow patterns that are difficult to predict using traditional flow models. Heinemann et al. (2021) emphasized the need for multidisciplinary approaches to model hydrogen storage at multiple scales, incorporating laboratory experiments, field data, and numerical simulations to address complex interactions between hydrogen and porous media [26]. Indeed, advances in multiphysics modeling platforms such as PHREEQC, CMG-GEM, DuMux, and others have enabled the integration of gas-phase reactions, microbial kinetics, geochemical changes, and fluid flow for the simulation of long-term UHS performance.

4.5. Challenges and Limitations

The insights gained from recent advancements in biogeochemical modeling underscore the complexity of microbial and geochemical interactions within UHS systems and also highlight strategic areas for research and development. Key issues are scaling the description of microbial and geochemical interactions from the small scale to the reservoir scale and the validation of the predictions against field data. Unlike controlled laboratory environments, underground reservoirs are subject to pressure changes due to gas injection and withdrawal, varying nutrient availability due to rock heterogeneity, and even temperature gradients due to cold fluid injection, which can drastically alter microbial activity, making it difficult to transfer laboratory-derived microbial growth rates directly to large-scale models.

4.5.1. Non-Linear Scaling of Microbial Processes

One major challenge is the non-linear scaling of microbial processes. While pore-scale and laboratory experiments can provide empirical data on microbial kinetics, these findings often fail to scale accurately to the complexities of real reservoirs. Microbial populations in subsurface environments exhibit behaviors that are not easily replicated in a lab setting. For example, the competition among microbial species, spatial heterogeneity in nutrient availability, and varying geochemical conditions can influence the rates of hydrogen consumption. Hogeweg et al. (2022) directly addressed this issue by comparing the performance of open-source and commercial simulators (DuMux, Eclipse only for the fluid-dynamic part) in their ability to model microbial methanogenesis under varying reservoir conditions [89]. The study found that while both simulators were capable of capturing general hydrogen trends, they produced discrepancies in the temporal prediction of microbial dynamics. This emphasizes the need for improved field data, as well as the refinement of model parameters to account for the highly variable nature of reservoir environments. Similarly, Wu et al. (2023) examined the discrepancies between laboratory-based microbial growth rates and simulated microbial activity at the reservoir scale [87]. Their study pointed out that nutrient availability, a critical factor influencing microbial growth, affects hydrogen consumption rates in ways that are not easily predicted by laboratory data. The authors also highlighted temperature gradients and pressure variations as important variables that can alter microbial behavior, further complicating the ability to scale laboratory models to reservoir-scale models.

4.5.2. Biofilm Formation at the Reservoir Scale

Another challenge is the difficulty in modeling biofilm formation at the reservoir scale. While the effect of biofilms has been well-documented in small-scale studies, modeling their long-term formation and spatial variability across an entire reservoir remains a challenge. For instance, Song et al. (2024) used pore-scale simulations to demonstrate that biofilm growth significantly reduces permeability, but its impacts can vary widely due to spatial heterogeneities [77].

4.5.3. Kinetic Variability in Long-Term Simulation

Models struggle to accurately represent the kinetic variability of microbial species over extended periods. Microorganisms like methanogens, acetogens, and sulfate reducers each have distinct reaction rates and growth patterns that can shift in response to changing environmental conditions [52]. The stochastic nature of microbial population dynamics adds further complexity, as certain microbial communities may dominate under particular geochemical conditions, only to be outcompeted by other species when those conditions shift [25,26]. This dynamic interplay between microbial species is difficult to capture within the deterministic frameworks that many large-scale reservoir models employ.

4.5.4. Field-Scale Experimental Validation

Eventually, field-scale validation remains one of the most significant barriers to advancing biogeochemical modeling for UHS. While controlled experiments and small-scale simulations provide important insights, their relevance to real-environment applications is limited by the absence of extensive field data. Thus long-term monitoring of UHS sites is critical for validating and improving modeling capability and accuracy [52].

4.6. Multi-Scale Modeling Workflow

Future research should focus on enhanced multiphysics modeling platforms and the development of new methods for scaling biological processes from pore-scale to reservoir-scale. Currently, some of the challenges posed by multi-scale modeling can be addressed by adopting the workflow suggested in Figure 1. In this workflow, the modeling begins at the pore and laboratory scales and progressively extends to the reservoir scale, with each step introducing new layers of complexity.

At the small scale, modeling efforts are primarily focused on capturing the detailed dynamics of microbial growth and geochemical reactions, biofilm evolution, and multiphase flow within porous media, which require experimental data collected under controlled laboratory conditions. Input parameters include microbial kinetic parameters (e.g., Monod kinetics for microbial growth and decay), geochemical properties such as mineral composition and reaction kinetics (e.g., hydrogen–mineral interactions and dissolution/precipitation rates), petrophysical data including porosity and permeability, relative permeability and capillary pressure curves for hydrogen and water, biofilm growth kinetics, and their effects on pore clogging. Furthermore, parameters such as wettability, surface tension, and fluid viscosity are critical for modeling hydrogen flow under reservoir-representative conditions. Additionally, environmental conditions, such as temperature, pressure, and formation water composition (e.g., dissolved organic and inorganic compounds), are essential. Experimental data from microfluidic experiments, batch reactors, and small-scale flow setups are used to validate these inputs.

At this scale, the modeling efforts are informed by laboratory experiments where controlled conditions allow the simulation of temperature, pressure, and pH in ways that replicate subsurface conditions. One of the most critical aspects at this stage is the use of microbial kinetic parameters such as Monod kinetics or other rate expressions that describe microbial growth and substrate utilization. These parameters are directly linked to microbial activities, such as hydrogen consumption, byproduct formation (e.g., methane, hydrogen sulfide, VFA), biofilm development, and mineral transformation. The outputs provide insights into microbial hydrogen consumption rates, byproduct formation, and changes in reservoir porosity resulting from mineral dissolution or precipitation and biofilm formation. These small-scale models can be validated against laboratory experiments, ensuring accurate calibration of reaction kinetics and microbial growth parameters.

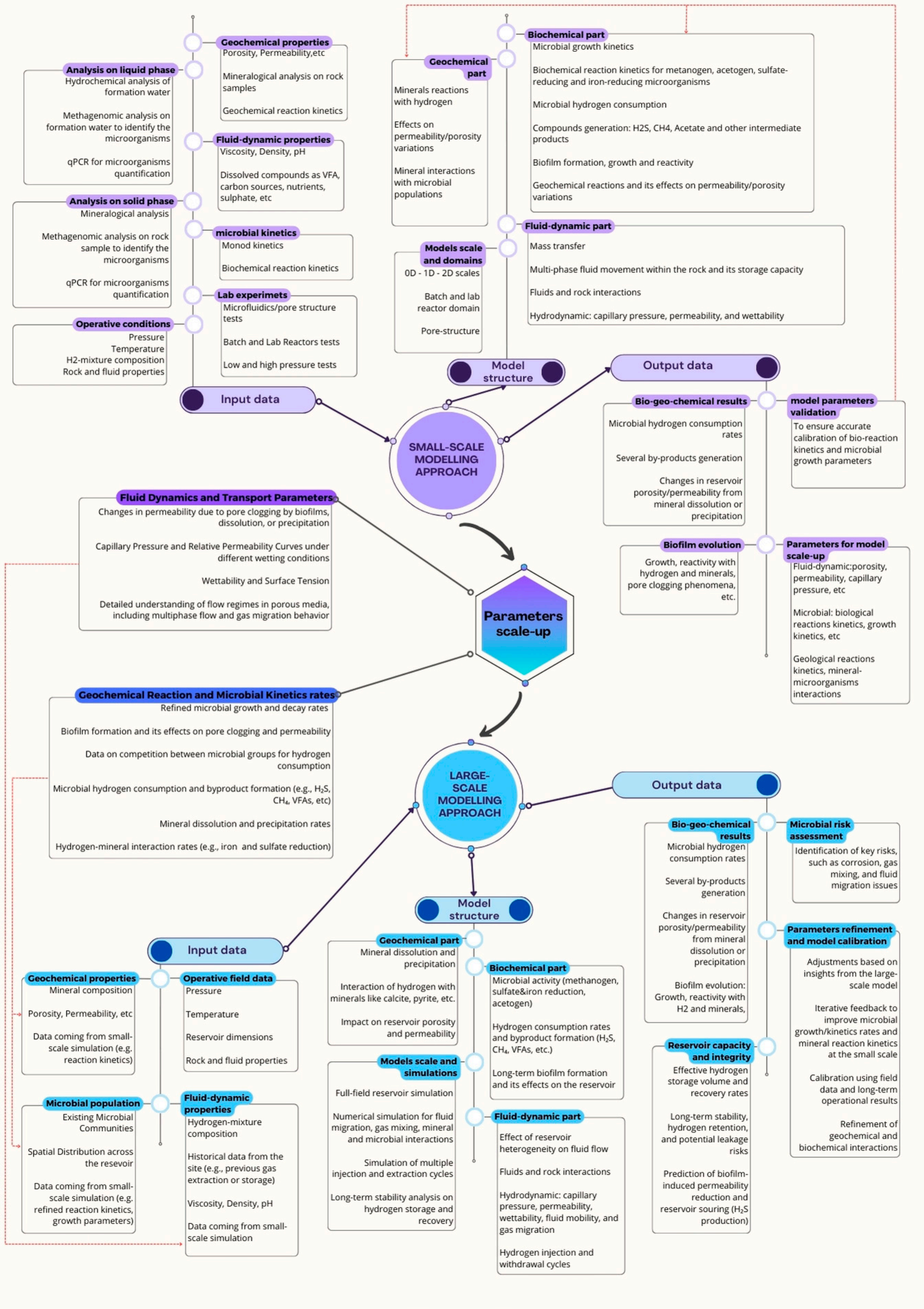

Figure 1. Workflow for biogeochemical modeling from small to reservoir scale.

As models expand to the intermediate scale, the focus shifts towards capturing the interactions between microbial populations and fluid dynamics across larger spatial regions. Here, the heterogeneity of the system, both in terms of geological features and microbial distribution, begins to play a crucial role. This heterogeneity affects fluid migration and the distribution of hydrogen, as well as the availability of electron acceptors like sulfate or carbon sources. Inputs for these models include the refined biogeochemical kinetic rates from small-scale simulations, the spatial distribution of minerals, microbial activity, and fluid properties. Outputs provide valuable information on hydrogen flow, the evolution of microbial communities, and the interaction between biochemical reactions and fluid migration through the porous media.

Reservoir-scale models aim to provide a comprehensive simulation of hydrogen flow dynamics and storage performance over long time scales. Thus, models must incorporate a more comprehensive set of inputs, reservoir-scale rock properties (e.g., bulk porosity and permeability), microbial population characteristics, geochemical reaction rates (e.g., sulfate reduction, methanogenesis), and site-specific environmental conditions, such as reservoir pressure and temperature gradients. These parameters are often scaled up from laboratory experiments and validated through site-specific geological surveys and field trials. Additional data include fluid dynamics properties (e.g., hydrogen and water mixture composition and flow rates) and the effects of long-term hydrogen injection and extraction cycles on reservoir integrity. These inputs ensure that large-scale simulations capture the heterogeneity and complexity of real reservoir systems.

The output from these large-scale models is the assessment of the storage site performance, including hydrogen retention, gas flow, and potential risks such as biofilm-induced permeability reduction or reservoir souring due to the generation of compounds such as hydrogen sulfide. Table 6 categorizes input parameters reported in Figure 1 according to the modeling scale (small scale and field scale) and highlights their purpose in numerical simulations. Parameters include microbial kinetics, geochemical properties, petrophysical data, and environmental conditions essential for simulating processes such as microbial activity, multiphase flow, and large-scale hydrogen storage dynamics.

A continuous feedback loop exists between the models at the small and large scales, where insights gained from large-scale models help refine the parameters and processes modeled at smaller scales. The integration of these scales is achieved through a rigorous iterative process that ensures consistency and accuracy across different levels of modeling. At the heart of this approach lies the use of fine-scale findings, such as microbial growth kinetics, pore geometry alterations, and mineral reaction rates, to parameterize and refine models at larger scales. For instance, pore-scale simulations provide critical insights into biofilm growth dynamics and localized permeability reduction, which are then upscaled to derive effective properties like porosity and relative permeability for core-scale models. Similarly, core-scale models, validated through experimental data, bridge the gap by incorporating localized heterogeneities and biofilm-induced effects into reservoir-scale simulations.

At the reservoir scale, the complexity increases as models must account for large-scale geological heterogeneities, such as fracture networks, variations in lithology, and site-specific environmental conditions (e.g., pressure and temperature gradients). These simulations establish boundary conditions for finer-scale models, ensuring that predictions at the pore and core scales remain representative of real-world reservoir behavior. Feedback loops between scales are essential. Reservoir-scale simulations, for instance, can identify regions of interest where finer-scale processes may dominate, prompting further refinements at the pore or core level. This iterative exchange of information ensures a cohesive representation of the system, where key processes at one scale inform and constrain the behavior at others.

Table 6. Summary of key input parameters collected from laboratory experiments for numerical modeling of UHS.

Modeling Scale	Input Parameters from Lab Experiments	Purpose in Numerical Models
Small Scale	Microbial kinetics: Monod parameters (growth and decay rates), substrate consumption rates, competition dynamics.	To capture detailed microbial growth dynamics, geochemical reactions, and changes in porosity and permeability due to biofilm formation or mineral reactions.To simulate multiphase flow in porous media and capture geochemical interactions at the core scale.
	Geochemical properties: mineral composition, reaction kinetics (e.g., hydrogen–mineral interactions, dissolution/precipitation rates).	
	Petrophysical data: porosity, permeability, formation water composition (e.g., dissolved compounds like H_2S, VFAs, CH_4).	
	Environmental conditions: temperature, pressure, rock–fluid properties.	
	Multiphase flow data: relative permeability and capillary pressure curves for hydrogen–water systems.	
	Biofilm kinetics: growth dynamics, pore clogging effects.	
	Wettability, surface tension, and fluid viscosity data.	
Reservoir Scale	Rock properties: bulk porosity, permeability distributions, mechanical integrity.	To evaluate reservoir-scale hydrogen storage dynamics, assess the impact of heterogeneity on hydrogen flow and reactivity, and ensure system integrity over time.
	Microbial activity: population thresholds, hydrogen consumption rates (e.g., sulfate reduction, methanogenesis, etc.).	
	Environmental conditions: reservoir temperature and pressure gradients.	
	Fluid dynamics data: hydrogen–water mixture composition, flow rates, injection/extraction cycles.	
	Long-term geochemical reaction rates and mineral stability data.	

This multi-scale, multi-factor modeling framework is critical for capturing the complex interplay of biological, chemical, and physical processes in UHS. For instance, microbial biofilm growth at the pore scale, which alters permeability, can propagate its effects to core-scale flow regimes, ultimately influencing reservoir-scale hydrogen mobility and storage efficiency. The framework also allows for the assessment of long-term storage performance by simulating the cumulative effects of microbial activity, geochemical reactions, and multiphase flow under varying operational scenarios.

Despite significant challenges that are not yet fully addressed, namely the non-linear scaling of microbial processes, the complex interactions between biological and geochemical phenomena, and the inherent heterogeneity of subsurface environments, this iterative multi-scale approach ensures that models remain robust and adaptable across different scales and provides improved simulation of UHS systems.

5. Conclusions and Future Perspectives

Recent advances in biogeochemical modeling have enabled the simulation of feedback loops between microbial activity and geochemical reactions and the description of the intricate biological dynamics that influence UHS systems. Studies have shifted from merely acknowledging microbial hydrogen consumption to thoroughly examining how microbial communities, biofilm formation, multiphase transport mechanisms, biogeochemical coupling, and mineral interactions co-evolve in the subsurface and affect hydrogen storage efficiency and reservoir integrity.

To further advance biogeochemical modeling for underground hydrogen storage, several key aspects should be prioritized in future research. One of the most pressing areas is the improvement of microbial growth models. While Monod-based models have provided a foundation for understanding hydrogenotrophic microbial activity, there is a growing need for more dynamic and adaptive models. Such models should be capable of capturing the feedback mechanisms between microbial growth and environmental changes such as temperature, pressure, pH, and geochemical reactions. By incorporating multisubstrate growth models, which account for microorganisms relying on multiple electron acceptors such as hydrogen, sulfate, or carbon dioxide, we can achieve a more accurate simulation of microbial behavior over the long term.

Another critical area for future work is that of scaling small-scale models to reservoir-scale applications. While pore-scale models provide valuable insights into localized microbial and geochemical processes, they often fail to accurately predict the behavior of large-scale systems due to the spatial heterogeneities and complexity of real-environment reservoirs. The workflow presented in this paper is a first attempt to approach multi-scale modeling and link detailed local processes with field-scale dynamics. However, additional efforts should be made to develop a consistent platform where critical data from laboratory experiments, field trials, and pilot projects can be integrated to account for microbial growth rates, gas consumption, production of byproducts such as methane or hydrogen sulfide, and complex geochemical processes, such as mineral dissolution and precipitation. To this end, collaborative efforts between experimental and modeling areas should focus on developing comprehensive databases of kinetic parameters and microbial behaviors across different geological settings. These datasets could help calibrate and validate models, ensuring that simulations align with real conditions.

Looking to a more distant future, an important direction for research will be the systematic quantification of uncertainties within these models. By conducting uncertainty quantification and sensitivity analyses, researchers would be able to identify the most influential parameters and prioritize areas that require accurate data collection. This would help improve the robustness of models and ensure the capability of accounting for the inherent variability and unpredictability of subsurface environments. Introducing stochastic modeling techniques could further enhance the ability to predict system behavior under different operational scenarios.

Lastly, the development of predictive tools that not only simulate processes but also help to mitigate risks in UHS systems will be critical. Models should be designed to provide operators with actionable insights for preventing issues such as gas loss, reservoir souring, or reduced recovery efficiency. Integrating machine learning algorithms into modeling frameworks could further enhance predictive capabilities, allowing models to learn from large datasets and offer reliable forecasts for long-term storage stability. Moving forward, collaboration between microbiologists, geochemists, reservoir engineers, and data scientists will be essential. By working together, these experts can build more comprehensive models, ensuring the safety and efficiency of UHS operations.

Ultimately, advancing biogeochemical modeling for UHS will support the broader goal of using hydrogen as a reliable and sustainable energy storage solution, helping to balance supply and demand in a renewable energy future.

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