Advances in the Mechanisms, Influencing Factors, and Control of Hydrogen Loss during Underground Hydrogen Storage in Depleted Reservoirs

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Abstract: *Underground hydrogen storage is key to achieving large-scale energy storage, managing the intermittency of renewable energy, and promoting the global energy structure's transition to low carbon. This paper reviews various hydrogen losses occurring during hydrogen storage in depleted gas reservoirs, categorizing hydrogen loss into chemical reactions, hydrogen flow, and hydrogen capture. It deeply discusses the loss mechanisms and key influencing factors of each type of loss. The results show: (1) Chemical reactions of hydrogen in the reservoir lead to permanent hydrogen loss, mainly influenced by reservoir mineralogy and microbial sensitivity; (2) Diffusion, viscous fingering, and leakage are the main factors of hydrogen flow loss, with attention needed on the integrity of the caprock and production facilities during storage; (3) Hydrogen loss due to dissolution capture is minor, but residual and adsorption capture can cause significant hydrogen loss under the influence of wettability, interfacial tension, capillary pressure, and phase trapping. Based on this, specific recommendations are provided to reduce hydrogen loss, and future research directions are outlined.*

Keywords: Underground hydrogen storage; Depleted gas reservoir; Hydrogen loss.
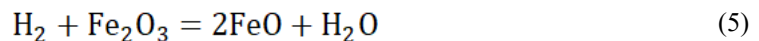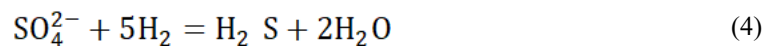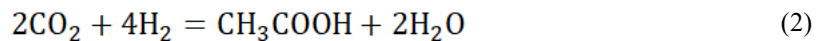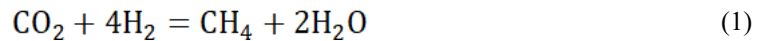
1. INTRODUCTION

The global energy structure is transitioning towards low carbon, and hydrogen energy, with its high energy density and low carbon emissions, has become a key energy source in this transition. In response, many countries and regions worldwide have successively formulated hydrogen development plans and raised higher requirements for hydrogen storage and extraction. Underground hydrogen storage has become a research focus due to its large storage capacity, high safety, and economic benefits. Among these, depleted gas reservoir hydrogen storage, with advantages such as clear geological conditions, abundant storage sites, and good matching with hydrogen production locations, has become the preferred choice for large-scale underground hydrogen storage. However, current understanding of hydrogen loss during hydrogen storage in depleted gas reservoirs is unclear, seriously affecting large-scale hydrogen storage and recovery, and hindering the development of large-scale hydrogen energy storage. To reduce hydrogen loss and improve storage efficiency, this study surveys domestic and international underground hydrogen storage technologies, analyzes hydrogen loss pathways during storage, discusses the loss mechanisms and key influencing factors in detail, analyzes existing research deficiencies and challenges, and proposes loss reduction suggestions for different types of losses, while looking forward to future research trends [1].

2. CHEMICAL REACTIONS

2.1 Biochemical Reactions

Hydrogen, due to its reducing properties, serves as an energy source for various microbial communities through different metabolic pathways. When methanogenic archaea coexist with carbon dioxide, they consume hydrogen to reduce carbon dioxide into methane, as shown in reaction (1). Acetogenic bacteria can metabolize hydrogen and carbon dioxide to produce acetic acid; the decomposition of acetic acid then generates methane and carbon dioxide, which cyclically promotes methane formation, as shown in reactions (2) and (3). Sulfate-reducing bacteria facilitate the reaction between sulfate ions and hydrogen to produce hydrogen sulfide, as shown in reaction (4). Hydrogen sulfide is an acidic and toxic gas that not only contaminates reservoirs and corrodes injection and production equipment but may also cause toxic gas leakage incidents. Iron oxide minerals in the formation also react with hydrogen under the catalysis of iron-reducing bacteria. For example, trivalent iron oxide reacts with
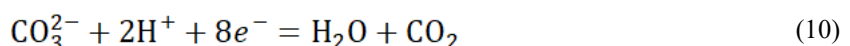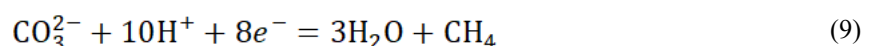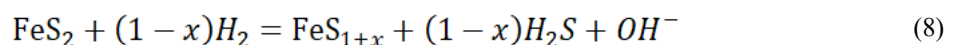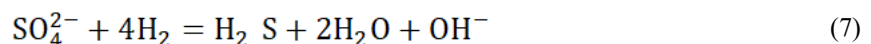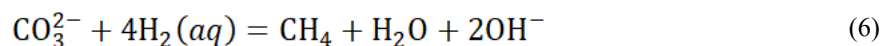
hydrogen to form divalent ferrous oxide and water, as shown in reaction (5). Iron-reducing bacteria also promote the dissolution of reservoir minerals, altering reservoir porosity and permeability, thereby affecting reservoir integrity. All the above reactions produce water, which occupies gas storage space, increasing the difficulty of hydrogen extraction and reducing the reservoir's hydrogen storage capacity. Moreover, when large numbers of microorganisms aggregate and proliferate, they form biofilms on rock pores or pipeline surfaces, further promoting mineral precipitation and corroding injection and production equipment, causing blockage of porous media pores or pipelines. This phenomenon often occurs near the bottom of injection and production wells, not only reducing the reservoir's storage and flow capacity but also diminishing the injection and production capacity of equipment, significantly lowering hydrogen storage efficiency.

$$CO_2 + 4H_2 = CH_4 + 2H_2O \tag{1}$$

$$2CO_2 + 4H_2 = CH_3COOH + 2H_2O \tag{2}$$

$$CH_3COOH = CH_4 + CO_2 \tag{3}$$

$$SO_4^{2-} + 5H_2 = H_2S + 2H_2O \tag{4}$$

$$H_2 + Fe_2O_3 = 2FeO + H_2O \tag{5}$$

The amount of hydrogen loss in these reactions varies significantly. Some researchers have found that the hydrogen content in mixed gases extracted from gas storage facilities decreases by 20–25%, while others have observed hydrogen losses as high as 40% due to microbial metabolism producing methane and hydrogen sulfide. However, after investigating 42 depleted oil and gas reservoirs in the UK, the Norwegian North Sea, and the Irish Sea, some scholars found hydrogen losses of only 0.01–3.0%, with methanogens causing an annual hydrogen loss of 0.6%. These findings indicate that the relationship between hydrogen loss and microbial activity is not clear-cut and mostly depends on the availability of substrates for microbial metabolism or the microbial population itself [2].

2.2 Geochemical Reactions

Under depleted gas reservoir conditions, minerals such as carbonates, sulfates, sulfides, and iron oxides are highly sensitive to hydrogen. The cyclic injection and production of hydrogen will promote geochemical reactions between hydrogen and reservoir minerals. For example, calcium carbonate in carbonate calcite dissolves in water to form carbonate and bicarbonate ions, which then react with aqueous hydrogen to generate methane, as shown in reaction (6). Sulfate minerals such as gypsum, anhydrite, celestite, and barite react with hydrogen to produce hydrogen sulfide, as shown in reaction (7). Sulfide minerals such as pyrite and marcasite react with hydrogen to form greigite, pyrrhotite, and hydrogen sulfide, as shown in reaction (8). These reactions cause mineral dissolution or precipitation, triggering significant hydrogen dissociation, altering reservoir porosity and permeability, and affecting the reservoir's injectivity and productivity. Some researchers have found that calcite and gypsum cement in the caprock dissolve in hydrogen-containing and 10%NaCl solutions, resulting in hydrogen loss while increasing the caprock's porosity and permeability.

$$CO_3^{2-} + 4H_2(aq) = CH_4 + H_2O + 2OH^- \tag{6}$$

$$SO_4^{2-} + 4H_2 = H_2S + 2H_2O + OH^- \tag{7}$$

$$FeS_2 + (1-x)H_2 = FeS_{1+x} + (1-x)H_2S + OH^- \tag{8}$$

$$CO_3^{2-} + 10H^+ + 8e^- = 3H_2O + CH_4 \tag{9}$$

$$CO_3^{2-} + 2H^+ + 8e^- = H_2O + CO_2 \tag{10}$$

The hydrogen loss rate caused by geochemical reactions is not low. Researchers have established kinetic models for the dissolution and precipitation of calcite and dolomite to evaluate hydrogen storage in carbonate reservoirs, finding that hydrogen-rock interactions lead to a hydrogen loss rate of 6.6%,500 in the first year, increasing to 81.1% after several years. Furthermore, they believe that hydrogen loss mainly occurs through hydrogen

dissolving into formation water to form aqueous hydrogen, which dissociates and participates in redox reactions. The dissociation equilibrium of aqueous hydrogen is close to a low pH environment, and higher pH leads to more hydrogen dissociation. However, other researchers have found that dry calcite also reacts with hydrogen to produce methane. Additionally, some scholars have found that hydrogen dissociation caused by calcite dissolution can lead to hydrogen losses as high as 9.5%, accompanied by carbon dioxide generation, and consider these reactions exothermic, with more intense reactions and faster hydrogen ion consumption at low temperatures, as shown in reactions (9) and (10). Numerical simulation studies related to geochemical reactions indicate that carbonate reservoirs perform poorly under long-term hydrogen exposure and are more suitable for seasonal short-term hydrogen storage. In contrast, sandstone reservoirs exhibit good stability, with weaker geochemical interactions with hydrogen, making them suitable for long-term large-scale hydrogen storage [3].

3. HYDROGEN FLOW

3.1 Diffusion in the Storage and Caprock

Hydrogen has a small molar mass (2.016 g/mol), and under the driving forces of chemical potential gradient, concentration difference, and gravity, it diffuses very easily in the formation, causing significant losses through the caprock and leakage points. Researchers used tracers with diffusion coefficients similar to hydrogen to simulate the diffusion of hydrogen and its related products in a faultless caprock with 5% porosity, finding that over 30 years, hydrogen loss due to diffusion in water was 2%, increasing with fingering occurrence, and leakage loss through the caprock did not exceed 25%. Subsequently, more scholars obtained similar results. However, some found that hydrogen diffusion loss in a caprock with 10% porosity was higher, reaching 5.5%, and they also suggested that hydrogen diffusion loss is functionally related to caprock porosity, diffusion coefficient, caprock gas saturation, and the area of caprock exposed to hydrogen. Nevertheless, others indicated that about 0.05% of hydrogen leaks into a caprock with permeability $10^{-5} \sim 10^{-3}$ mD during hydrogen storage, about 1% dissolves into water, but hydrogen dissolution in the aquifer and diffusion loss in the caprock can be reduced to within 0.1%.

Hydrogen is a low-viscosity fluid, with viscosity at normal temperature and pressure only 8.90×10^{-3} mPa·S , and it easily undergoes viscous fingering in multiphase flow within formations. Some researchers found that viscous fingering usually occurs perpendicular to the fluid flow direction, which increases the contact area between hydrogen and formation rock and fluids, promoting hydrogen dissolution and diffusion, but it is suppressed by high porosity, high permeability, and low injection rates. Studies on hydrogen and methane migration in anticline structures under different injection rates found that at low injection rates, gravity dominates and the gas-water interface uniformly descends, with the cross-section basically horizontal; at moderate injection rates, gravity and viscous forces jointly cause lateral gas diffusion beneath the caprock, with only slight descent of the gas-water interface at the structural center; at high injection rates, viscous forces become the main factor, and the gas-water interface only descends early in injection, followed by extensive lateral fingering [4].

3.2 Leakage of Production Facilities

Hydrogen leakage losses in production equipment are mainly caused by equipment aging and wellbore integrity damage, including microbial corrosion of production casing, hydrogen blistering and hydrogen embrittlement of steel, cement degradation, and packer aging failure. Among these, microbial corrosion is still caused by sulfate-reducing bacteria and iron-reducing bacteria. When sulfur is present, sulfate-reducing bacteria consume hydrogen to produce hydrogen sulfide, which corrodes the metal casing surface and increases the amount of hydrogen penetrating the steel. When minerals such as iron oxide, organic carbon, or montmorillonite are present, redox reactions occur on the metal surface under the action of iron-reducing bacteria. Hydrogen blistering of steel is mainly caused by hydrogen atoms chemically adsorbing dissociatively on the metal surface; atomic hydrogen accumulates in surface depressions, increasing pressure and leading to plastic deformation. When the supply rate of hydrogen atoms exceeds their dissolution rate, it may cause metal rupture, resulting in leakage risk. After hydrogen penetrates the steel surface, under lower stress and higher hydrogen concentration and pressure, hydrogen bubbles can also cause hydrogen-induced cracking. Brittleness is mainly due to hydrogen molecules diffusing into the steel's microstructure, which may exacerbate hydrogen-induced cracking.

Hydrogen losses caused by microbial corrosion, steel hydrogen embrittlement, and hydrogen blistering are not

significant; conversely, cement degradation and packer failure may lead to greater hydrogen leakage. First is mechanical degradation of cement: due to the porosity and permeability characteristics of cement, under high-intensity pressure fluctuations and thermal expansion and contraction, cement is prone to mechanical degradation and even crack formation, causing hydrogen to permeate through the cement layer and result in losses. Second is chemical degradation of cement: when carbon dioxide or hydrogen sulfide is present, carbonation and sulfidation reduce cement strength and generate cracks. Packers are seals that isolate fluids in casing, tubing, or annular control, typically composed of a main steel body and elastic rubber. During ultra-high-pressure cyclic injection and production of hydrogen, elastic materials are easily damaged by rapid pressure changes, allowing hydrogen to penetrate inside and form blister cracks. Additionally, elastic materials undergo chemical degradation in environments containing carbon dioxide, hydrogen sulfide, or caustic alkalis, resulting in brittle fracture surfaces [5].

4. HYDROGEN CAPTURE

4.1 Dissolution Capture

Depleted gas reservoir formations typically contain formation water with high mineralization. After hydrogen injection, prolonged contact with formation water inevitably leads to dissolution phenomena. Experiments on the dissolution of hydrogen in pure water and brine have been quite extensive, covering a variety of reservoir temperatures, pressures, and salinity conditions. Some researchers have measured the solubility of hydrogen in pure water under 50°C and 100°C conditions to be between $5\sim30\times10^{-4}$ mol/Kg, and found that it increases with rising pressure. However, even under extreme conditions of 200°C and 100MPa, the solubility of hydrogen in pure water is only 1.6×10^{-3} mol/Kg. Additionally, measurements of hydrogen solubility in brines of varying mineralization within the temperature range of $0\sim120$°C revealed that high mineralization suppresses hydrogen solubility; when brine mineralization increases from 5000ppm to 35000ppm, hydrogen solubility decreases from $0.8\sim1.6\times10^{-3}$ mol/Kg to $0.2\sim0.4\times10^{-3}$ mol/Kg. Subsequent studies have reached similar conclusions. Some researchers have quantified hydrogen loss due to dissolution during hydrogen storage, finding that when hydrogen is fully saturated, the connate water occupying 20% of the pore volume causes a 0.4% loss of injected hydrogen, and over a six-month injection-production cycle, hydrogen loss through dissolution in the reservoir aquifer is less than 1%[6].

4.2 Residual Trapping

The cyclic injection and production of hydrogen causes part of it to be trapped in narrow pore spaces or inside capillaries, forming residual trapping. Especially in reservoirs with strong heterogeneity and complex pore-throat distributions, it is easy to form water-sealed gas in the form of blockage or migrate to low-permeability zones. When capillary forces are strong and hydrogen wettability is low, a large amount of hydrogen cannot be recovered. Core displacement experiments by some scholars found that when hydrogen injection drainage is conducted at a slow rate, hydrogen can occupy about 65% of the sandstone pore volume. After gas displacement by brine, the residual gas saturation in the core reaches as high as 41%, showing significant residual trapping loss. With the increase of formation pore volume, the loss caused by residual trapping tends to rise. When pore pressures are 2, 5, and 7 MPa, hydrogen losses caused by secondary swelling reach 20%, 22%, and 43%, respectively. Some scholars evaluated the hydrogen storage capacity of clay-rich sandstone and found that during gas displacement of water, only 16% of hydrogen replaced water in large pores. After water displacement of gas, trapping mechanisms caused 14% residual hydrogen, with hydrogen loss rates exceeding 95%, possibly due to the strong water-wet nature of clay minerals leading to more residual trapping. Other scholars used the co-injection steady-state method for relative permeability experiments and found that after the first displacement cycle, when the gas phase relative permeability was 0.049, the residual gas saturation was 0.4, indicating that residual trapping caused nearly 40% hydrogen loss, but this phenomenon weakens with increasing cycle numbers. Additionally, some scholars conducted hydrogen-water multiphase flow characterization experiments on heterogeneous Berea sandstone cores and found that during swelling, due to the unstable displacement front of fluids, finger-like flow with high water saturation was formed. The linear trapping coefficients inside and outside the finger channels of the core were 0.085 and 0.77, respectively, averaging 0.44, leading to substantial hydrogen trapping loss.

Phase permeability hysteresis causes residual trapping to be influenced not only by the critical gas saturation but

also by the saturation history, and the cyclic injection and production in underground hydrogen storage reservoirs affect the saturation history. In a scholar's five-cycle injection-production simulation experiment, hydrogen loss due to residual trapping was 30.1%, 25.1%, 20.6%, 17.1%, and 14.5%, respectively. They indicated that phase permeability hysteresis does not affect hydrogen dissolution trapping, but neglecting phase permeability hysteresis leads to an overestimation of recovered hydrogen and associated water content. Moreover, the larger the area invaded by the hydrogen plume, the greater the proportion of hydrogen trapped residually. Numerical simulation studies by other scholars also show that during underground hydrogen storage in saline aquifers, although the hysteresis of gas-water two-phase relative permeability increases the purity of produced hydrogen, it also reduces the hydrogen recovery rate [7].

4.3 Adsorption Trapping

Hydrogen adsorption loss is mainly caused by high pressure; due to its slow desorption rate, which is much lower than the adsorption rate, it often fails to meet industrial recovery requirements, resulting in certain hydrogen losses over a short period. Research on gas adsorption-desorption is mostly focused on coalbed methane and shale gas, with relatively less on hydrogen. Scholars systematically studied the adsorption capacity of clay minerals such as montmorillonite, illite, chlorite, sepiolite, and kaolinite using high-pressure adsorption isotherms and the Langmuir model, finding that montmorillonite exhibits severe adsorption hysteresis, leading to nearly 42.19% hydrogen storage loss, followed by sepiolite with a 3.56% loss. The adsorption capacities of hydrogen, nitrogen, methane, and carbon dioxide increase progressively. Montmorillonite shows significant volumetric expansion during adsorption, which may be the main cause of severe adsorption hysteresis. Therefore, the relationship between mineral structural changes during adsorption-desorption and hysteresis loss requires further clarification. Additionally, they found that the adsorption process of some minerals under high pressure is thermodynamically non-spontaneous, indicating that high temperature is unfavorable for adsorption.

Some scholars used gas chromatography to determine the adsorption of gaseous hydrogen by sodium synthetic montmorillonite-type clay and CO_x-type clay. Experiments found that after dry clay samples reacted with hydrogen for 30-45 days under relative pressures of $90^\circ C$ and 0.045MPa, hydrogen of 0.11% was adsorbed on the clay, and the adsorption amount decreased with increasing temperature. In numerical simulations using molecular dynamics models to describe hydrogen adsorption in carbonate (limestone calcium carbonate) reservoirs, it was found that under conditions of $400\sim600K$ and 0.1MPa, the adsorption amount of hydrogen on the calcium carbonate rock surface reached 0.42%, increasing with the specific surface area. Obviously, the rock's hydrogen adsorption capacity is highly sensitive to temperature and pressure. It should be noted that adsorption may overlap with chemical reactions between hydrogen and the rock (e.g., hydrogen reacting with iron at high temperatures), leading to inaccurate adsorption data. Especially in cases where adsorption increases with rising temperature, purified rock should be used to exclude chemical reactions that may be more temperature-sensitive. Furthermore, gas adsorption and desorption may cause rock deformation, resulting in changes in specific surface area, permeability, and mechanical properties. Factors affecting hydrogen adsorption under in-situ formation conditions require further study [8].

5. CONCLUSION

Achieving the highest storage efficiency with minimal storage loss is the goal and requirement for the development of underground hydrogen storage technology. Based on the above discussion and analysis, the following conclusions and recommendations are drawn:

(1) Geochemical and biochemical reactions of hydrogen under reservoir conditions cause a permanent loss of 0.01% to 25% of hydrogen in the reservoir. These reactions lead to mineral dissolution or precipitation in the reservoir, altering the sealing capacity of the cap rock or clogging the reservoir. Additionally, by-products such as methane, hydrogen sulfide, carbon dioxide, and water generated by these reactions not only significantly reduce hydrogen recovery rates but also contaminate the reservoir and lower the purity of recovered hydrogen. Therefore, selecting sandstone reservoirs with stable properties, using microbial inhibitors, and reducing substrates that support microbial metabolism are effective measures to reduce such hydrogen storage losses.

(2) The high diffusivity of hydrogen causes its diffuse loss in the reservoir; its diffusion loss in water is usually less

than 5%, but leakage loss through the cap rock can reach up to 25%. Hydrogen diffusion in the reservoir is mainly influenced by pressure and injection rate, especially high-speed injection which may lead to severe viscous fingering. Therefore, controlling a reasonable injection rate and formation pressure is key to reducing hydrogen diffusion, viscous fingering, and leakage loss through the cap rock. Leakage of hydrogen through production facilities is minor, but a comprehensive diffusion and leakage monitoring system should still be established, along with regular equipment performance monitoring and quality maintenance to prevent leakage incidents.

(3) The trapping mechanism can cause 20% to 95% hydrogen storage loss, mainly affected by wettability, interfacial tension, capillary pressure, and phase permeability hysteresis. Although related experimental studies have been relatively extensive, most experiments have been conducted on artificial materials, and experiments under in-situ formation materials and conditions remain to be carried out. Additionally, more core-scale gas-water two-phase displacement experiments are needed to provide more accurate fundamental data for numerical simulation and engineering research.

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