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Evaluating Geochemical Reactions for Hydrogen Storage in Salt Caverns

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Summary

Large-scale production of hydrogen (H_2) necessitates the development of efficient storage facilities. Among underground storage options, salt caverns are widely regarded as the most favorable due to the low permeability of salt rock, its ductile behavior, and the minimal cushion gas required [1–3]. However, many salt formations worldwide contain impurities and non-salt layers formed during their depositional period, including anhydrite, carbonates, silicates, and clay minerals. These impurities can significantly influence the mechanical properties of salt rock and its geochemical interactions with brine and H_2 [4–6]. Despite ongoing research, the interactions between impure salt rock media and H_2 or H_2/brine systems remain poorly understood. This study extends the understanding of salt-rock behavior by investigating the effects of H_2 in the brine-salt rock systems under underground hydrogen storage conditions. Batch reaction experiments were conducted using impure salt rocks from the Lotsberg Formation and its overlying caprock in Fort Saskatchewan area, Alberta, to evaluate the impact of H_2 on mineral dissolution and precipitation processes in salt caverns. Additionally, kinetic geochemical modeling was performed using the PHREEQC software to simulate geochemical reactions within the H_2-brine-salt system, accounting for mineral dissolution and microbial activity.

Theory / Method / Workflow

First, we conducted batch reaction experiments using a high-pressure high-temperature (HPHT) reactor to simulate salt rock-brine-H_2 systems and investigate potential geochemical reactions in the absence of microbial activity. The reactor was filled with selected salt rocks, a water phase, and H_2 gas. A combination of analytical techniques, including X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and gas chromatography (GC), was employed to monitor changes in the salt rock, water, and gas phases before and after the experiments. These experiments provided insights into the geochemical reactivity of H_2 with impure salt rocks and enabled an assessment of the effects of hydrogen H_2 on mineral dissolution and precipitation. Specifically, we evaluated changes in mineral composition, ion concentrations in the brine, potential secondary mineral formation, and the generation of gaseous by-products. Following the experimental work, kinetic modeling was performed using the PHREEQC software to simulate geochemical reactions in the H_2-brine-salt system, incorporating the effects of various mineral dissolutions and microbial activities. The model was validated against published experimental data and subsequently used to predict long-term hydrogen consumption and by-product generation in salt caverns.

Results, Observations, Conclusions

The experimental results indicated that abiotic redox reactions are unlikely to occur in H_2-brine-salt rock systems. Silicate minerals, such as K-feldspar and quartz, exhibited negligible dissolution and no reactions with H_2. In contrast, anhydrite and carbonate minerals, such as calcite and dolomite, showed slight dissolution, with anhydrite dissolving at the highest rate. The findings revealed that H_2 does not significantly influence mineral dissolution or precipitation under these conditions, with predominant non-reductive dissolution reactions occurring in the carbonate minerals. As shown in Figure 1, the XRD results confirm that the presence of H_2 does not affect the dissolution or precipitation of salt-rock minerals under the experimental conditions. Furthermore, the absence of gaseous by-products and the unchanged ion concentrations in the solution provide further evidence that no redox reactions involving H_2 occurred.

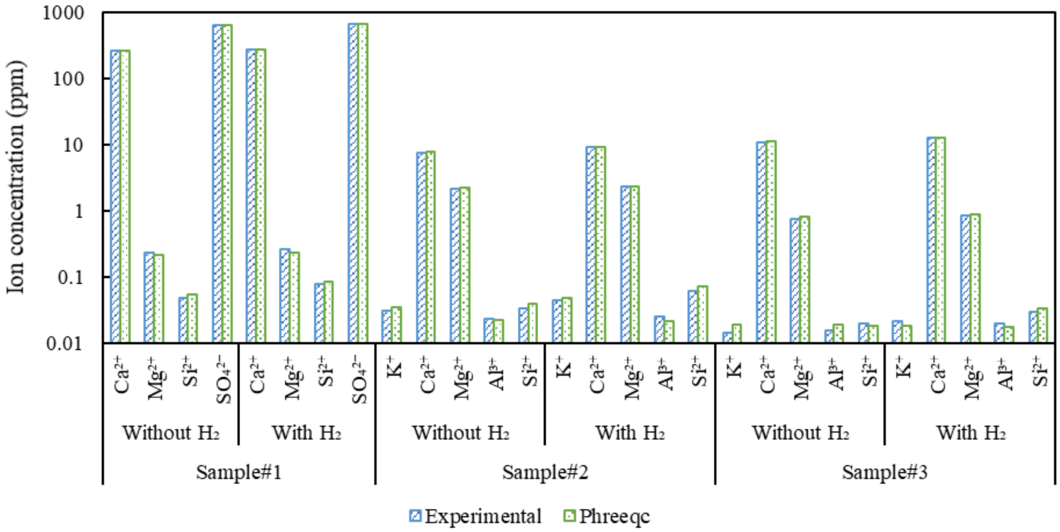


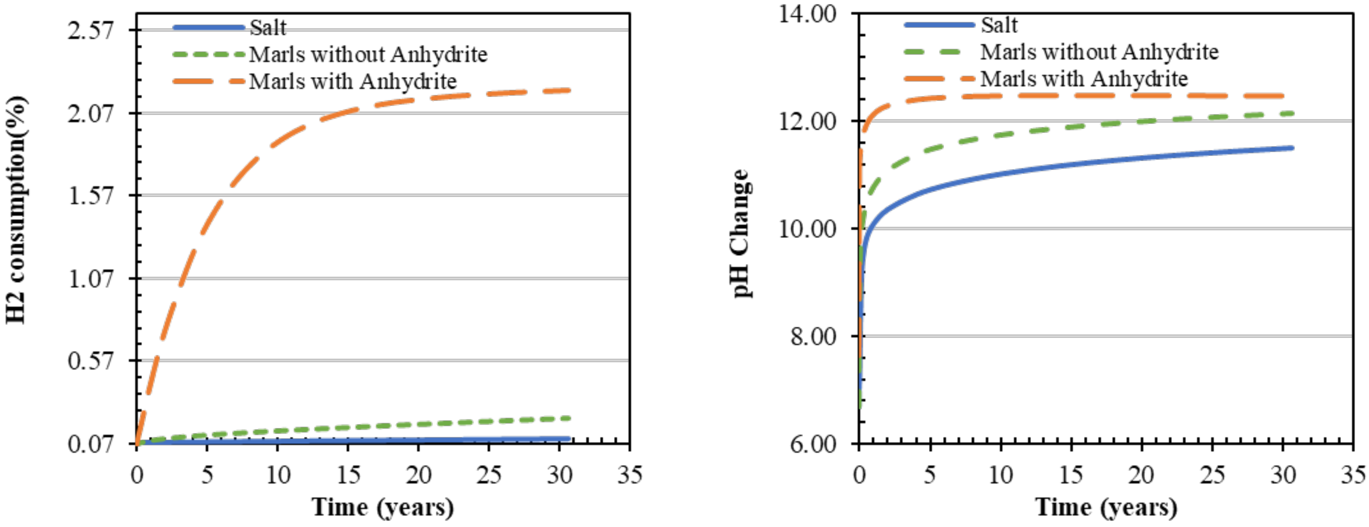
Figure 1. Measured and modelled ion compositions for rock-water systems after batch reaction experiments.

However, under actual storage conditions, biotic reactions must be considered due to the potential presence of sulfate-reducing and methanogenic bacteria. The modeling results indicate that in systems containing carbonates or anhydrite, microbial activity can trigger redox reactions. Dissolved sulfates and carbonates may be reduced by H_2, potentially producing CH_4 and H_2S, which in turn enhance mineral dissolution and H_2 consumption. Kinetic modeling that incorporates both mineral dissolution rates and microbial activities (methanogenesis and sulfate reduction) identifies anhydrite as a critical mineral influencing hydrogen purity. The mineral composition of the salt rock plays a pivotal role in determining hydrogen consumption and gas generation. As shown in Figure 2, in the Lotsberg Salt system, which primarily consists of halite, H_2 consumption remained very low (0.08%) over 30 years. In contrast, a marlstone system containing anhydrite exhibited significantly higher hydrogen consumption (2.1%). The pH of the systems increased over time, attributed to redox reactions between H_2 and dissolved sulfate (SO_4^{2-}) and carbonate (CO_3^{2-}).

Novel/Additive Information

The experimental and modeling results enhance the understanding of geochemical reactions between H_2, salt rocks, and brine in salt caverns. They also provide insights into potential H_2

consumption and by-product generation during long-term H_2 storage in salt caverns, offering valuable guidelines for optimizing H_2 storage.



(a) (b)

Figure 2. The hydrogen consumption and pH change during a 30-year period for Lotberg salt, marlstone with anhydrite and marlstone without anhydrite: (a) H_2 consumption (%), (b) pH change. These modelling results consider both mineral dissolution rate and the kinetic methanogenesis and sulfate reduction by microbes.

Acknowledgements

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Reference Style (use Arial 9pt normal)

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