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Geochemical Effects of Hydrogen Storage in Unlined Rock Caverns: A Modelling Study Using Limestone as the Host Rock

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Abstract **-** Underground Hydrogen Storage (UHS) is a promising option for achieving large-scale renewable energy storage, and unlined rock cavern (URC) storage is an attractive alternative to conventional UHS options. Limestone could be a potential host rock for the construction of the URC. However, to confirm the viability of the limestone, a better understanding of the reactivity of hydrogen-brine-limestone systems is necessary. Therefore, we conducted a geochemical modelling study to explore the interaction between hydrogen and limestone. This investigation involved kinetic batch modelling under environmental conditions typical of shallow-depth unlined rock caverns (URCs). During the 100-year simulation, carbonate minerals like calcite, dolomite, magnesite, and siderite wholly dissolved due to redox reactions with hydrogen. As a result, over 80% of the hydrogen was lost, leading to methane (CH_4) gas production. However, these reactions were driven by methanogenesis, which is known to be kinetically limited under the low temperatures (40^0) used in this study and needs to be catalysed through, e.g. by the microorganisms. Consequently, we adjusted the database to focus solely on abiotic reactions. Under these conditions, hydrogen exhibited behaviour akin to inert gas, showing negligible reactivity. In the absence of catalysed redox reactions, limestone emerges as a robust choice for URC construction. However, microorganisms in URCs could potentially catalyse these reactions, rendering limestone unsuitable for URC construction.

Keywords**:** Underground hydrogen storage, Unlined rock caverns, Geochemical modelling, Carbonate reactivity

1. Introduction

Transitioning from fossil fuels to renewable energy sources is imperative for a more sustainable future. In this transition, hydrogen (H_2) emerges as a promising low-carbon energy carrier capable of mitigating the variability in energy production associated with renewable sources. By harnessing surplus energy during periods of excess, hydrogen can be generated via electrolysis, stored, and later released to meet energy demands during deficits[1, 2]. Underground hydrogen storage (UHS) in geological formations, including salt caverns, depleted hydrocarbon reservoirs, and aquifers, has been proposed as a highly viable solution for large-scale hydrogen storage as these formations can store hydrogen at the GWh/TWh scale [3, 4]. Unlined Rock Caverns (URCs) are another potential UHS method offering storage capacities and cycles comparable to salt caverns. Moreover, URCs are artificially constructed using conventional mining techniques, providing the advantage of selecting sites near renewable energy sources such as solar and wind farms, which are anticipated to supply energy for hydrogen production[5, 6].

In URCs, the rock walls are in direct contact with the stored hydrogen. Consequently, it is important to consider potential geochemical reactions within the H_2-groundwater-rock system that may impact the chemical composition, petrophysical properties, and geomechanical behaviour of the host rock. According to Allen et al.[7], who proposed guidelines for URC construction, granite, granodiorite, quartzite, massive gneiss, dolomite, and limestone, are the most suitable candidate host rock types for URCs. Recent studies have explored the reactivity of calcite in the presence of hydrogen, particularly considering the occurrence of calcite minerals in reservoir rocks[8-12]. However, most existing studies have primarily focused on deep reservoir conditions (temperatures > 75^0C), and to date, no investigations have specifically examined the impact of hydrogen storage on limestone host rocks under the milder conditions expected in shallower (less than 1 km depths[5]) URC storage scenarios. Furthermore, despite most geochemical modelling studies indicating significant hydrogen losses, methane (CH_4) generation, and calcite dissolution in carbonate-hydrogen reactivity[11, 12], experimental studies often report minimal reactivity, and hydrogen behaves similarly to that of inert gas[8, 9].

This study aims to numerically assess the potential geochemical reactions between hydrogen and limestone host rocks in the context of hydrogen gas storage within unlined rock caverns. Hence, kinetic batch models were developed for potential URC storage pressure (10 MPa), temperature (40^o) and salinity (5% NaCl) conditions. The models were developed using PHREEQC geochemical software (V.3.7.3 from US Geological Survey) [13]. The impact of hydrogen presence was assessed by simulating both hydrogen-brine-limestone and brine-limestone models. Furthermore, it has been recognized that adjustments to the thermodynamic databases used in numerical modelling are necessary to account for the inert behaviour of hydrogen observed in experimental studies. The impact of these modifications on hydrogen-limestone reactivity was subsequently evaluated.

2. Methodology

2.1. Sample Description

The limestone samples for this study were obtained from a borehole (Woolwoola 25) in the Murray Basin, Australia at a depth of 165 meters. The Drill Core Library of Victoria provided these samples. To facilitate the mineral composition data input into the PHREEQC analysis, X-ray diffraction (XRD) analysis was conducted on the limestone samples using the Bruker D8 Cobalt instrument at Monash University. The resulting mineral composition, quantified via the PDF-5+ database in the DIFFRAC EVA 4.3 software, is presented in Table 1.

Table 1. Mineral composition of the limestone sample

Mineral	Weight Percentage %	Mineral amount in the simulation (mol/kgw) assuming 0.1 kg of limestone
Calcite	76.7	0.76639
Kaolinite	10.9	0.04222
Quartz	9.6	0.15976
Siderite	1.3	0.01122
Dolomite	0.7	0.00380
Magnesite	0.8	0.00949

2.2. Modelling Scenarios

All the simulations were conducted assuming a batch experiment, as shown in Figure 1. Here, 1 kg of brine (5% NaCl) and 0.1 kg of limestone were placed in a hypothetical reaction chamber and were pressurised with 1 L of hydrogen at a pressure of 10 MPa and a temperature of 40^oC. All the conditions were selected to best represent the shallow underground conditions encountered in a URC. To distinguish the impact of dissolved hydrogen on limestone from that of brine, we initially constructed the following two distinct geochemical models:

I. Hydrogen-brine-limestone
II. Brine-limestone (without the presence of hydrogen)

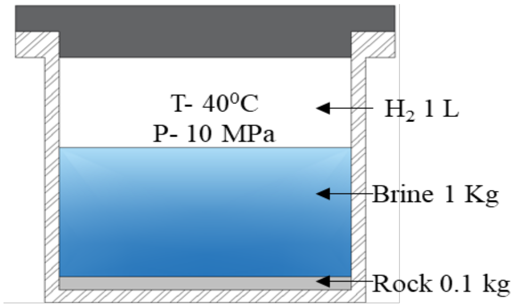

Fig 1. Assumed kinetic batch simulation conditions

2.3. Kinetic Batch Modelling

All the models were built as kinetic batch models simulating over 100 years to evaluate the geochemical interaction between H_2 and limestone using the phreeqc.dat database. These simulations focus on Hydrogen consumption and mineralogy changes at each time step, considering temporal constraints and reaction kinetic rates of minerals within the system.

The kinetic reaction rate (r (mol/s)) for all the minerals except calcite and dolomite is calculated using the equation (1) given by Lasaga et al. [14]. Rate parameters for quartz and kaolinite were collected from Parkhurst and Appelo [13], while those for magnesite and siderite were obtained from Zhang et al.[15]. For calcite and dolomite, kinetic rates are defined by the expression proposed by Plummer et al. [16]. For further details on these rate equations, refer to the publication by Bo et al.[11]. The reactive surface area (RS_A) of the minerals was included in the simulation, assuming the mineral grains are spherical. All the minerals, except kaolinite, have an average grain diameter of 0.000033 m. For the kaolinite, an average grain diameter of 0.000002 m is taken[17].

$$r = kRS_A(1 - \left(\frac{Q}{K_e}\right)^{\theta})^{\eta} a_{H^+}^{n} \tag{1}$$

Where k is the rate constant (mol $m^{-2}s^{-1}$), RS_A is the reactive surface area (m^2 g^{-1}), $a_{H^+}^{n}$ is the aqueous activity of the H^+ ion, n is the order of the reaction, K_e is the equilibrium constant, and Q is the corresponding ion activity product. The θ and η are usually set equal to one.

3. Results and Discussion

3.1. Hydrogen Loss

The loss of stored hydrogen gas serves as a crucial indicator for assessing the efficiency of UHS. Under the storage conditions considered, at the end of one year, approximately 5% of the hydrogen was lost. By the 20-year mark, over half of the simulated hydrogen had been lost, and by the 100-year mark, more than 80% of the hydrogen was lost (as indicated by the "H_2 loss - unmodified database" in Figure 2). Within the URC environment, hydrogen may be lost either 1) through dissolution into the groundwater within the cavern bottom or 2) via geochemical reactions in the hydrogen-brine-limestone system. It is important to note that over 100 years, the dissolved hydrogen concentration remains at approximately 0.05 mol/kg, accounting for only about 1.5% of the initial hydrogen gas quantity. Therefore, it is clear that the significant hydrogen loss is primarily due to geochemical reactions, particularly involving carbonate minerals such as calcite, siderite, dolomite, and magnesite, as described by Equation 2. This observation is further supported by the formation of impurity gas CH_4, as indicated in Equation 2 and depicted in Figure 2. The potential generation of CH_4 could result in hydrogen gas contamination, and impact storage integrity and efficiency.

$$CO_3^{2-} + 4H_2 + 2H^+ \leftrightarrow CH_4 + 3H_2O \tag{2}$$

The geochemical models built by Bo et al.[11] and Zeng et al.[12, 18] observed similar observations of carbonate mineral reactivity with hydrogen, significant hydrogen losses, and CH4 gas generation. However, Al-Yaseri et al[9, 10] and

Gelencsér et al[8] did not make comparable observations in their experimental studies. The discrepancy may arise from the databases employed in numerical studies, such as phreeqc.dat, lnll.dat and core10.dat[8]. These databases include equation (2), which represents the thermodynamic reaction of methanogenesis—a process that is kinetically limited. However, at temperatures below 90°C (as anticipated in URCs), this reaction is likely catalysed by microorganisms[5, 18]. Notably, these microorganisms were not included in the experimental studies discussed, as those studies focused solely on abiotic conditions. Hence, to consider the effect of purely abiotic geochemical reactions, the phreeqc.dat database was modified by blocking the equation (3). This would prevent the formation of CH_4 gas.

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

The loss of hydrogen calculated with the modified database is depicted in Figure 2 as "% H_2 loss-modified database". Throughout the 100 years, the hydrogen loss is only around 1.5% of the initial hydrogen amount present, which is almost equal to the amount that is lost due to the dissolution. Hence, hydrogen behaves nearly like an inert gas and exhibits negligible geochemical reactions under the storage conditions examined in this study, if reactivity remains unaffected by the presence of a catalyst, such as microorganisms. However, there have been previous instances where the presence of microorganisms, particularly methanogenic Archaea, led to methanogenesis (equation (2)) and resulted in CH_4 generation in oil storage URCs [19]. Thus, in the presence of microorganisms, limestone may not be an ideal choice for constructing unlined rock caverns (URCs) intended for hydrogen storage. However, it's crucial to account for additional factors—such as nutrient availability and environmental conditions—that influence bacterial growth. While modelling these complexities numerically is challenging, it provides a more accurate representation of field conditions.

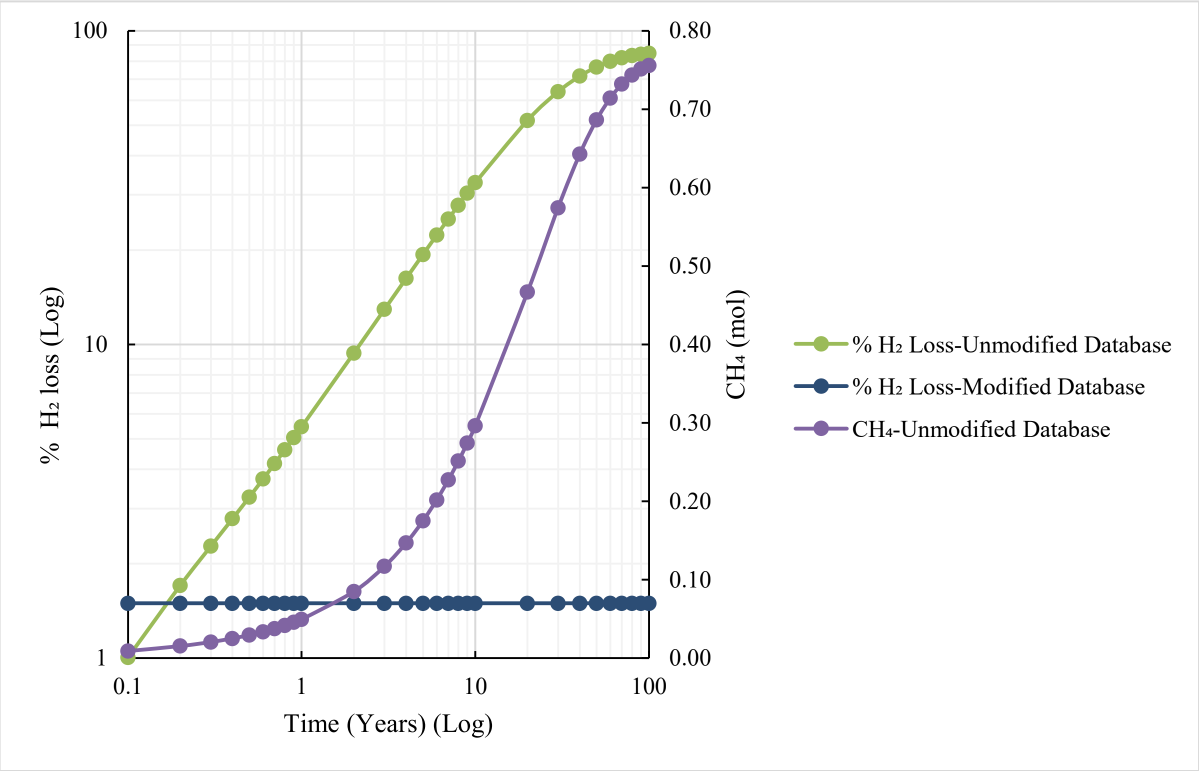

Fig 2. Hydrogen loss and CH_4 formation

3.2. Mineral Dissolution

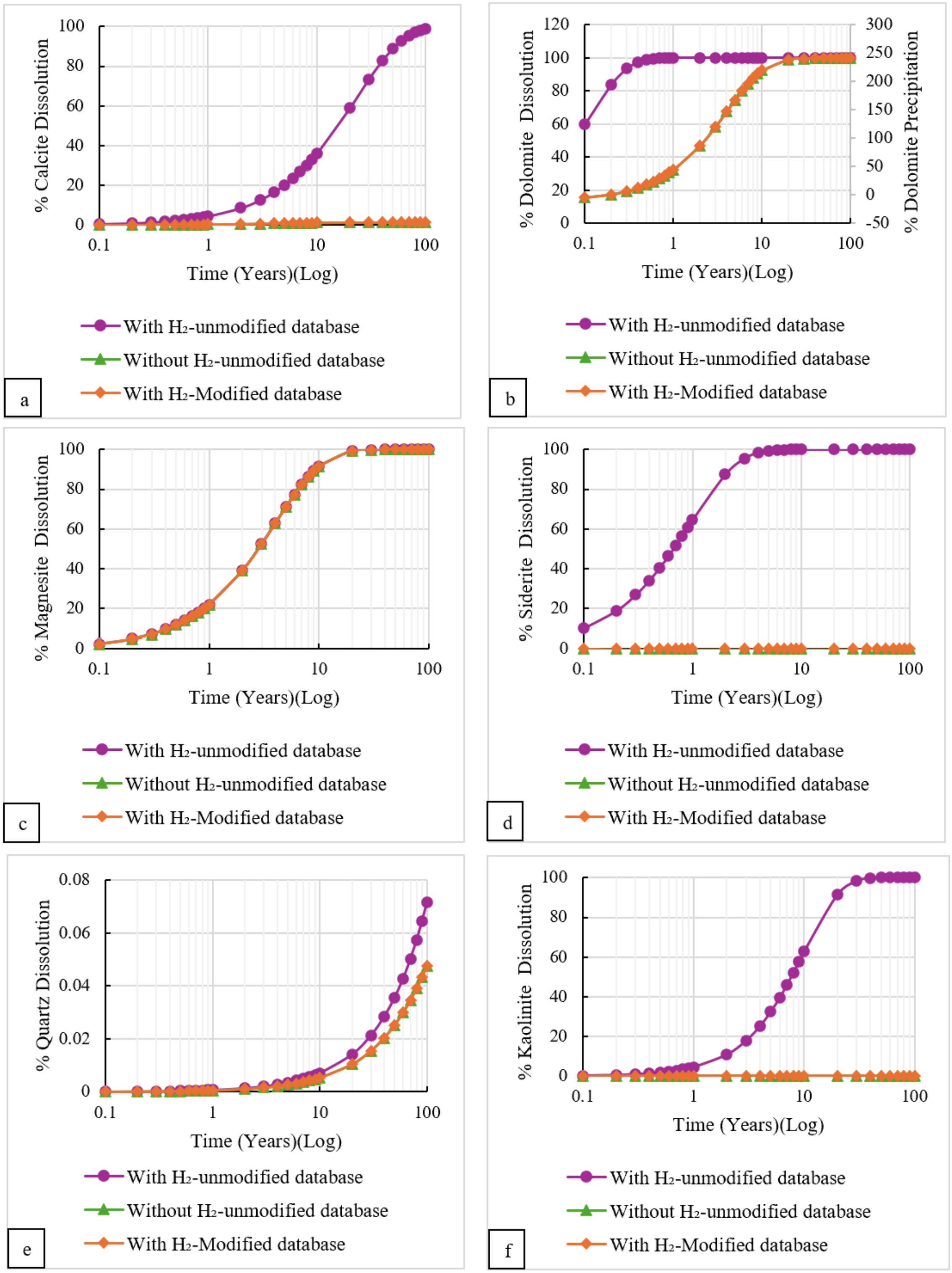

Fig 3. Mineral dissolution

In the unmodified phreeqc.dat database, carbonate minerals undergo complete dissolution over time according to the following timeline: Calcite dissolves by the end of 100 years (Fig 3(a)), dolomite within 1 year (Fig 3(b), magnesite within 60 years (Fig 3(c)), and siderite within just 10 years (Fig 3(d)), as described by equation (2). When the database is modified by removing equation (3), the dissolution behaviour of these carbonate minerals becomes similar to that observed without hydrogen, i.e. limestone-brine modelling scenario. Notably, the dissolution rates decrease significantly for most minerals, except for magnesite, which maintains the same dissolution rates regardless of the presence of hydrogen or modifications to the database. With the modified database, calcite dissolution is approximately 1% of its initial amount, while siderite dissolution accounts for only around 0.05%. Whether or not the database is modified, i.e. whether there are microorganisms present, quartz shows minimal dissolutions (less than 0.1% of the initial mol amount) in the presence of hydrogen. When considering kaolinite, the unmodified database undergoes complete dissolution within 90 years. However, with the modified database, kaolinite exhibits minimal dissolution (approximately 0.05%), resembling the behaviour seen in the scenario without hydrogen. This behaviour aligns with that of carbonate minerals. However, unlike carbonates, kaolinite is not a redox-sensitive mineral. Its dissolution is primarily triggered by the pH increase resulting from the redox reaction between hydrogen and the carbonate minerals[18].

4. Conclusion

Unlined Rock Caverns (URCs) are gaining prominence as an underground hydrogen storage solution. Carbonate rocks, including limestone and dolomite, are potential host rocks for constructing these caverns. Hence, this study explores the geochemical reactions that may arise between limestone, brine, and hydrogen, impacting their mineralogical, petrophysical, and geomechanical properties, ultimately affecting the cavern's integrity and storage efficiency. The kinetic modelling results revealed carbonate minerals such as calcite, dolomite and siderite could undergo complete dissolutions due to hydrogen. Furthermore, more than 80% hydrogen was lost in 100 years, as well as CH_4 gas is formed. However, these reactions were driven by methanogenesis, which needs to be catalysed by the presence of microorganisms under the URC low temperatures (40^o) modelled in this study. These reactions are kinetically limited, negligible, and similar to those without hydrogen scenarios (i.e. hydrogen behaves similarly to that of an inert gas) when the database is modified to account for only abiotic hydrogen reactions. Furthermore, it is identified that the dissolution of magnesite is initiated by brine alone, and the dissolution of kaolinite is triggered by the pH increase caused by the dissolution of the carbonate minerals.

Finally, it can be concluded that in the absence of catalysed redox reactions, limestone emerges as a robust choice for URC construction. However, it should be noted that, from the past storage experiences, in the actual URC conditions, microorganisms could be present driving the reported carbonate and hydrogen reactions in this study. However, field conditions introduce additional complexities, including nutrient availability and environmental factors affecting bacterial growth. To enhance accuracy, geochemical modelling should account for these factors. Furthermore, targeted laboratory investigations should explore the specific impact of microorganisms on carbonate rock-H_2 reactivity systems. Addressing this research gap will provide valuable insights into the suitability of carbonate rocks for hydrogen storage in URCs.

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