WA School of Mines: Minerals, Energy and Chemical Engineering

# Geochemical Modelling on $H_2$-Brine-Mineral Interactions and Its Implications on Hydrogen Loss and Caprock Integrity

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# Declarations

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University.

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# Abstract

Hydrogen energy appears to be an emerging energy carrier to achieve energy transition from traditional fossil fuel to renewables. In hydrogen development, underground hydrogen storage (UHS) in depleted hydrocarbon reservoirs is important to underpin the full-scale and long-term hydrogen economy supply chain. However, there has been a raising concern about the caprock sealing capacity in hydrogen storage process, since hydrogen as the smallest molecule with active chemical nature and is potentially diffusing away from caprock pores and also react with certain groups of minerals. Especially when there is pre-existing oxygen at subsurface, redox reaction is possibly intensified and causing excessive mineral consumption and hence impact caprock porosity and permeability, which leading to sealing failure. Some previous research has investigated the impacts of $H_2$-brine-mineral interactions on hydrogen loss with an absence of oxygen. It is stated that water uptake of hydrogen has insignificant reaction with silicate and clay minerals, and also temperature and pressure contribute minor roles in aqueous hydrogen loss. Nevertheless, there is lack of research aimed to the impact and implications of hydrogen-brine-mineral interactions on caprock sealing capacity (mineral consumption) with considering the presence of dissolved oxygen at subsurface. Therefore, it is of vital importance to examine the potential caprock seal capacity risks associated with hydrogen-brine-oxygen-mineral redox reaction in terms of hydrogen conversion and contamination, mineral dissolution, and hydrogen solubility.

Apart from hydrogen-brine-oxygen-mineral redox reaction, there is second scenario relating to caprock sealing capacity, which is diffusion/dispersion activity, since hydrogen has much higher diffusion coefficient. If hydrogen threshold pressure is low, reservoir pressure is highly possible to pump out the stored hydrogen gas through caprock formation and leading to unwanted hydrogen loss. However, very limited research has been done to focus on required caprock thickness to securely store large-scale hydrogen gas, and hydrogen loss in long-term storage. Thus, evaluation of caprock sealing capacity associated with dispersion activity in terms of hydrogen diffusion length, aqueous hydrogen loss is becoming to an essential part in underground hydrogen storage feasibility matrix.

To achieve two proposed objectives, we hypothesized that (1) geochemical interactions play a minor role in sandstone reservoirs with dissolved oxygen presenting at subsurface and will not impact to caprock sealing capacity. (2) Hydrogen dispersion activity may cause negligible hydrogen loss through caprocks giving its minor dissolution in brines, securing long-term hydrogen storage.

To test these two hypotheses, redox reaction and reactive transport diffusion geochemical modelling were established under certain assumptions, such as elevating pressure, temperature, and storage time. It is used to interpret caprock mineral dissolution, hydrogen conversion and contamination percentage, gas diffusion depth, and aqueous diffusion loss.

The results from redox reaction modelling indicate that dissolved oxygen at subsurface has negligible impact on mineral dissolution and hydrogen loss regardless of temperature, pressure and mineral types, due to the relatively low oxygen contents. As an anerobic condition at subsurface, pre-existing dissolved oxygen is insufficient to support intensified redox reaction with large scale of underground hydrogen storage. However, carbonates minerals such as calcite and siderite may trigger hydrogen loss from redox reaction, resulting in excessive methanogenesis in particular with microbials. Especially at low temperature range, all $HCO_3^-$ from carbonates dissolution has been converted to methane by reacting with hydrogen based on the existing geochemical database from PHREEQC (Version 3).

The results from reactive transport dispersion modelling show that hydrogen dispersion distance is no more than 60 cm under assumed temperature (25°C - 80°C) and pressure (100atm – 300atm) within 30 years of storage time, implying a low risk in hydrogen loss associated with hydrogen dispersion through caprock without pre-existing fractures.

# Acknowledgements

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# Acknowledgement of Country

I acknowledge that Curtin University works across hundreds of traditional lands and custodial groups in Australia, and with First Nation people around the globe. I wish to pay my deepest respects to their ancestors and members of their communities, past, present and to their emerging leaders. My passion and commitment to work with all Australians and peoples from across the world, including our First Nations people are at the core of the work we do, reflective of our institutions' values and commitment to our role as leaders in Reconciliation space in Australia.

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# Chapter 1. Introduction

## 1.1 Background

The world population growth and rapid urbanization cause strongly negative impact on traditional energy demand and climate change. The global population is predicted to reach 10 billion[1] in 2060 and the energy demand would increase to 770 exajoules[2] by end of 2060. The associated carbon emission is becoming an urgent issue to neutralize and eliminate. Therefore, energy transition from fossil fuel to renewables is the key to build up a new energy structure in the future. Hydrogen energy development is confirmed to be the most potential solution to achieve energy transition due to its zero-carbon emission and high energy density. However, to enable hydrogen value chain globally, a few knowledge gaps remain to be addressed. One of such is the development of large-scale hydrogen storage in a cost-effective and safe manner. It is reported that 2500 TWh is required for Europe by 2050[3], which requires roughly 28.34 billion surface tanks (such as, size 85L surface tank with 75Mpa)[4] for hydrogen storage, whereas current hydrogen storage capacity is limited to meet such large scale and fluctuated storage purpose. Thus, hydrogen underground storage in porous medium is drawing global attention to suits large scale hydrogen storage purpose.

There are a few areas relating to hydrogen underground storage feasibility assessment, such as hydrogen cycling performance in reservoirs[2], caprock integrity[5], hydrogen conversion and contamination[1]. They all possibly lead to existing geological structure alteration such as porosity permeability, and geological stress change, and hence causing unwanted hydrogen loss. Additionally, the geochemical interactions between hydrogen, brine and rock are associated with reservoir wettability, since most of subsurface porous medium is considered as water-wet condition, whereas the mixture of stored hydrogen gas and pre-existing cushion gas may alter relative permeability and capillary pressure, and further change the reservoir wettability condition, then resulting to storage failure[6]. Therefore, researchers have conducted reservoir wettability analysis and confirmed that the wettability is showing insignificant dependency on pressure temperature and salinity with experimental evidence from microfluidics[7], tilted plates[8], core flooding[9] and captive-bubble cell methods[10]. However, there is still lack of study on hydrogen loss through caprock resulting from hydrogen-brine-mineral interactions and hydrogen dispersion.

To gain a deeper understanding of hydrogen loss through caprock caused by hydrogen-brine-rock interactions, several driving mechanisms are proposed, such as gas solubility, mineral dissolution, aqueous gas loss, hydrogen conversion and contamination, and gas dispersion activity, which are all associated with rock porosity and permeability change. During hydrogen injection process, hydrogen gas is in contact with aquifer and caprock, hydrogen solubility in aquifer may varies with subsurface pressure and temperature change. Once sufficient hydrogen gas dissociates in subsurface brine, this hydrogen-brine-mineral contact possibly triggers geochemical redox reaction and causes certain groups of mineral consumption since hydrogen acting as strong reducing agents with its active chemical nature[3]. Especially when dissolved oxygen is detected at subsurface, redox reaction is possibly intensified and leads to significant mineral consumption and hydrogen loss[11]. Once drastic mineral dissolution taking place, mineral porosity and permeability is altered and caprock sealing capacity is likely weakened. Also, the dissolved hydrogen gas and precipitated mineral from redox reaction is displaced by aquifer flow, which leads to further aqueous hydrogen loss. Additionally, certain groups of minerals such as, $HCO_3^-$ and $SO_4^{2-}$ based minerals not only intensify geochemical reaction to causes mineral consumption, it also may significant hydrogen conversion and contamination[12], which also fails the hydrogen storage purpose. For example, produced $HCO_3^-$ from carbonate dissolution likely reacts with hydrogen ions to triggers methanogenesis[13]. This mineral dissolution process alters caprock porosity and permeability which may consequently reduce its sealing capacity and results to stored hydrogen gas leakage from dispersion activity, since hydrogen gas has relatively higher diffusion coefficient, and is likely escaping from high porosity and permeability rock formations[5]. Therefore, a pressing and urgent need are rising to quantitatively characterize the impacts and implications of hydrogen-brine-mineral interactions and hydrogen dispersion on caprock integrity in terms of hydrogen loss and mineral dissolution.

## 1.2 Research Objectives

This research aims to systematically quantify the impacts and implications of hydrogen-brine-mineral interactions and hydrogen dispersion on caprock integrity. To achieve this main objective, it is paramount to characterize (1) how the interactions between hydrogen, brine, dissolved oxygen and single minerals (e.g., quartz, calcite, pyrite, and siderite) affect caprock integrity in terms of porosity and permeability change from mineral dissolution, precipitation, and hydrogen loss (including, aqueous hydrogen loss, hydrogen conversion and contamination), and (2) quantify how hydrogen diffusion/dispersion activity contributes to hydrogen leakage through caprock. Based on above-described objectives, two main hypotheses have been proposed and listed as follow.

Hypothesis #1 – Impacts of dissolved oxygen plays minor role in underground hydrogen storage whereas carbonates minerals may trigger significant aqueous hydrogen loss and mineral dissolution, which may weaken wellbore integrity (increased porosity and permeability)

Hypothesis #2 – Hydrogen diffusion/dispersion activity causes minor hydrogen loss through caprock due to negligible dissolution of hydrogen in aqueous phase at reservoir pressure and temperature.

To test these hypotheses, geochemical modelling such as gas solubility, aqueous hydrogen loss and mineral dissolution, hydrogen diffusion were established to interpret the in-situ gas-brine-mineral interactions and associated with caprock integrity. Static batch model was developed for single mineral system to investigate the impacts of different mineral type on hydrogen loss, gas solubility and caprock integrity. Reactive transport model was designed for multi-mineral system to study the hydrogen diffusion loss and penetration depth through caprock without carbonates mineral presenting.

## 1.3 Thesis Structure

This thesis is mainly in consist of six chapters. Chapter 1 illustrates importance and urgency of conducting research works of geochemical interactions and hydrogen dispersion impacts on reservoir caprock integrity, clarifying the main engineering problems, two objectives and two hypotheses. Chapter 2 is detailed summarizing the literature review of $H_2$-brine-mineral interactions and hydrogen dispersion activity impacts on caprock and hydrogen loss that has been done. Chapter 3 is to frame the entire thesis and demonstrate detailed methodology, which addresses each objective and engineering problems.

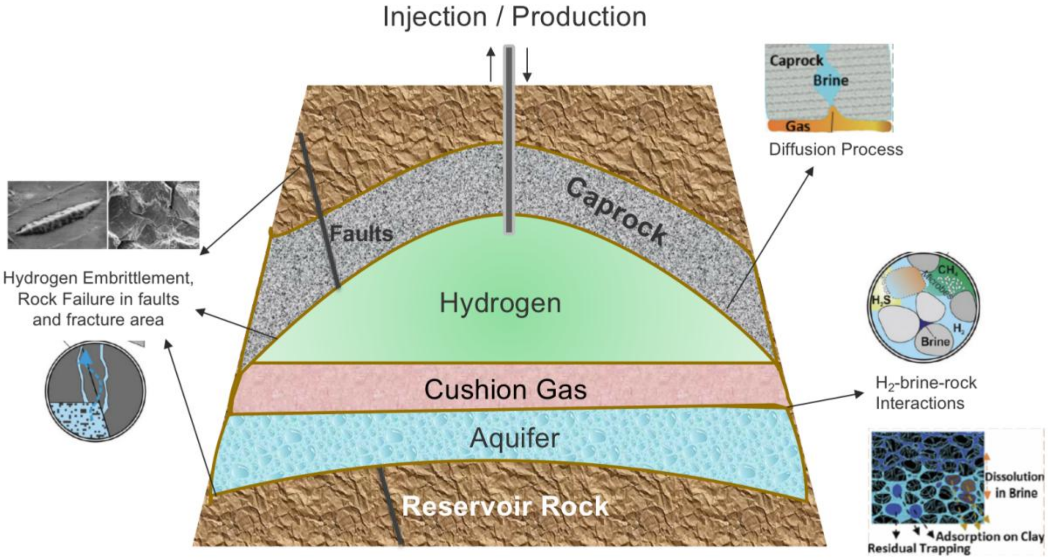
In chapter 4, several static batch modellings (PHREEQC Notepad++ Version 3)[14] were used to study the geochemical interaction impacts of different minerals on caprock integrity in terms of hydrogen loss, mineral consumption, pH variation and gas solubility. Then, results were interpreted into engineering implications to promote large-scale hydrogen storage globalization. In this chapter, the simulation modellings mainly focus on single mineral system under increasing pressure(0-1000atm) and temperature condition (20-200℃). Quartz, calcite, pyrite, and siderite were selected as the main testing sample. The result is showing that only carbonate minerals (calcite and siderite) contribute significant hydrogen loss and mineral consumption, which further cause caprock porosity and permeability change.

Based on the observation from Chapter 4, it is decided to select poor-carbonates reservoir data in Chapter 5 as the study object to conduct extensive research to quantify the impact of dispersion activity on caprock integrity. It is using PHREEQC Notepad++ Version 3 software[14] to establish a reactive transport model and assuming 30 years of hydrogen underground storage time. The results will show the gas diffusion depth and peak diffusion rate as the function of time, temperature, and pressure. Additionally, Chapter 6 covers future PhD project briefing, which is regarding to caprock geomechanical properties variation determination while hydrogen cycling process is applied.

# Chapter 2. Literature ReviewImpacts of $H_2$-brine-mineral interactions on hydrogen loss and caprock integrity

Caprock integrity is mainly defined as sealing capacity in underground hydrogen storage, which relates to original mineralogy, geomechanical structures, such as porosity and permeability [15]. In our case, the caprock integrity variation can be determined by mineral consumption during hydrogen storage process. Because if strong hydrogen-brine -mineral interactions taking place, not only causing unwanted hydrogen loss, but also dissolving certain groups of minerals from caprock formation, and further causes mineralogy and porosity change, and possibly leading to sealing failure.

Figure 2. 1 Underground hydrogen storage environment illustration figure.



There are a few summarized literatures have concluded two types of geochemical interactions contributing to caprock integrity, change and or hydrogen consumption, which are (1) biotic[16] and (2) abiotic[16]. Biotic process is regarding to living components at subsurface such as bacteria, germs, the several biotic reactions relating to hydrogen underground storage are named by sulphate reduction, iron reduction, methanogenesis, and acetogenesis[16]. They are all contributed to hydrogen conversion and contamination by consuming hydrogen and produce new gases and or precipitation. For example, in Lobodice town gas project[16], significant amount of unpredicted methane was generated by mixture of excessive hydrogen and carbon dioxide, which is shown in figure 2.2. They also hypothesized that for those Fe(III)-rich reservoirs, it is highly possible to trigger iron reduction process since hydrogen is considered as an active electron donor and causing $Fe^{3+}$ reducing to $Fe^{2+}$ and even solid iron[16]. However, these biotic reactions are likely to be involved abiotic process between subsurface brine, gas and certain groups of minerals. Although, abiotic process mainly considering nonliving components, there are some specific subsurface minerals can trigger above mentioned reactions without any microorganism presenting [15]. Once one or more reactions are triggered, the occupied fluids and gases tend to precipitate and or dissolve minerals. This mineral precipitation and dissolution rate is reported to be dependent on pressure, temperature, mineral type, and pre-existing ions[9]. If mineral dissolution rate is less than precipitation rate, caprock may remain intact, otherwise, porosity and permeability of caprock will be altered, as a result, its sealing capacity will be reduced, and hydrogen conversion and contamination will take place [17-19].

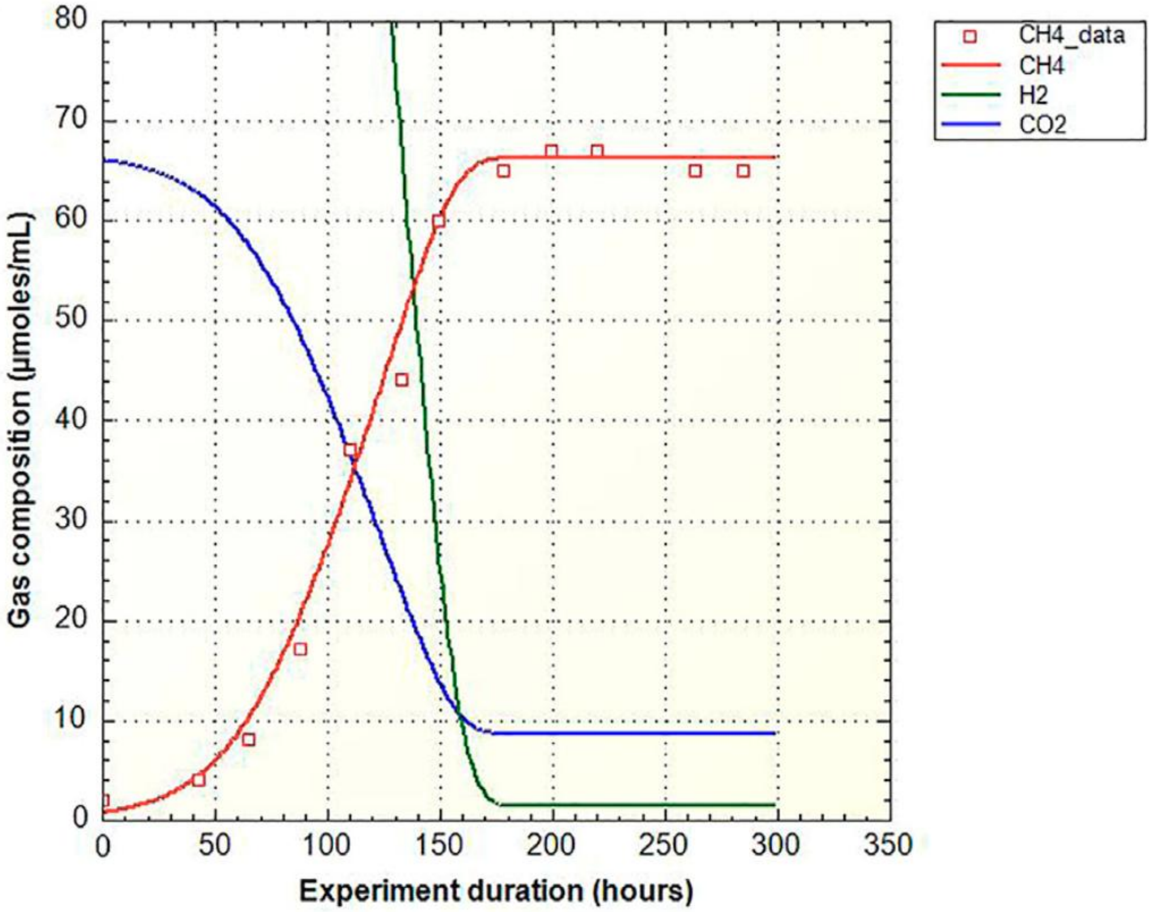


Figure 2. 2 methane production (squares) from hydrogen and carbon dioxide in presence of Lobodice rock and formation water containing bacteria (37°C, 1.5 bar) [16]

Furthermore, another factor that possibly intensifying the geochemical interactions is subsurface dissolved oxygen. It is reported that the dissolved oxygen content is ranging from 2ppm to 8ppm at depth of 100 - 1000 meters in the Ash Meadows ground-water basin, south-central Nevada, which is shown in figure 2.3. [20]. The presence of both oxygen and hydrogen gas likely intensify geochemical interactions in the form of redox reaction, because dissociated hydrogen can act as reducing agent and oxygen gas act as oxidation agent, the hydrogen-brine-mineral redox reaction will be completed with their buffering[21]. As a result, hydrogen dissociation will be triggered, hydrogen and mineral losses will be increases with alkaline environment forming. In this case, pH level will act as an important indicator to show the extent of redox reaction. For example, if hydrogen and oxygen support strong redox reaction with gas dissociation under a temperature and pressure increased condition, dissociated hydrogen ions in brine will be consumed and pH level will be increased, or pH remains at initial state with no free hydrogen ions amount change in solution, otherwise, pH decreases with excessive hydrogen ions dissociated in brine[22-25].

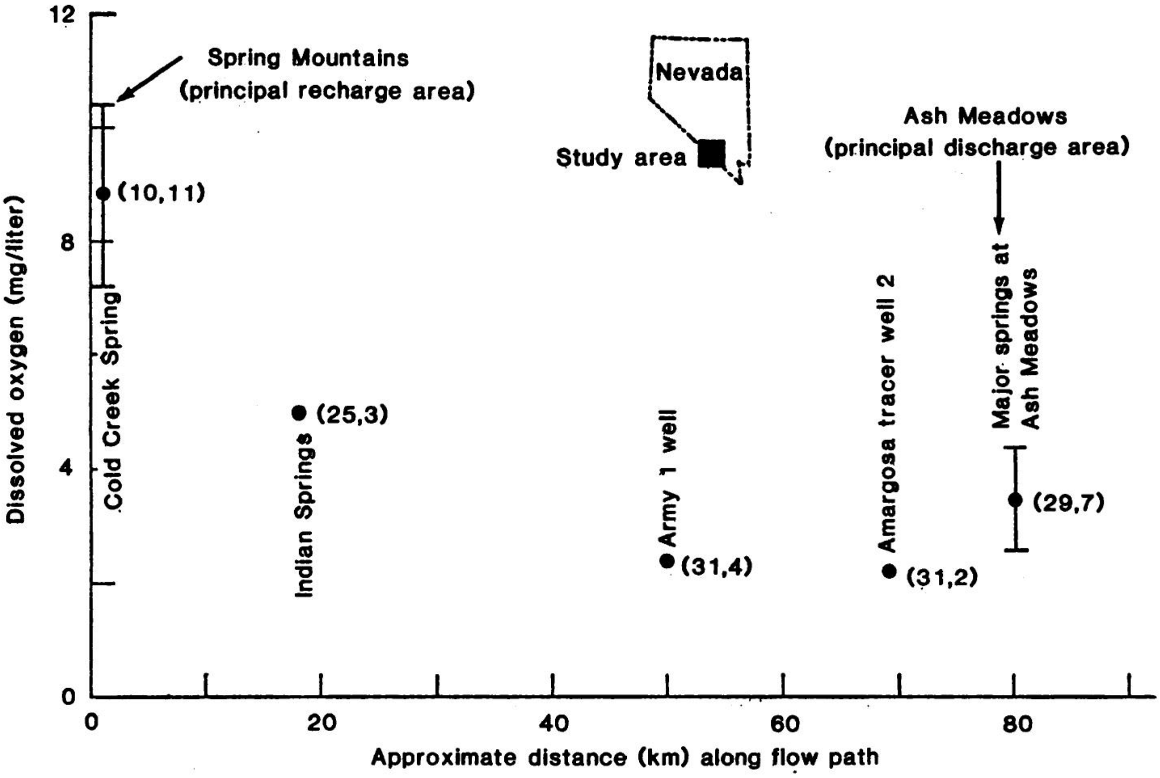


Figure 2. 3 Variation in the dissolved oxygen content of ground water along an approximately 80-km

flow path in the Ash Meadows ground-water basin, south-central Nevada. [20]

Although, there are some literatures investigated geochemical reaction effect on hydrogen underground storage, limited research has considered presence of dissolved oxygen and mineral loss of caprock formation. Therefore, it is of vital importance to quantify the impacts of geochemical reactions among hydrogen, dissolved oxygen, brine and different minerals (quartz, siderite, pyrite, and calcite) on caprock integrity and hydrogen conversion and contamination. Gas solubility in brine and pH level can be set as the indicator to monitor geochemical reactions behaviour on hydrogen and mineral losses.

## 2.2 Impacts of $H_2$ dispersion activity through caprock on hydrogen loss

The other factor that might affect caprock integrity is gas diffusion activity. It is defined as the net movement of a substance (e.g., ions, atoms, molecules, and energy) from a higher concentration region to a lower concentration region, which is driven by Gibb’s free energy or chemical potential[26, 27]. Molecular diffusion activity is commonly considered as a slow process whereas hydrogen molecular diffusion coefficient is relatively high ($5\times10^{-9}$ m$^2$/s)[28] in pure water at 25℃, which is still possible to impact caprock sealing capacity in long-term storage project.

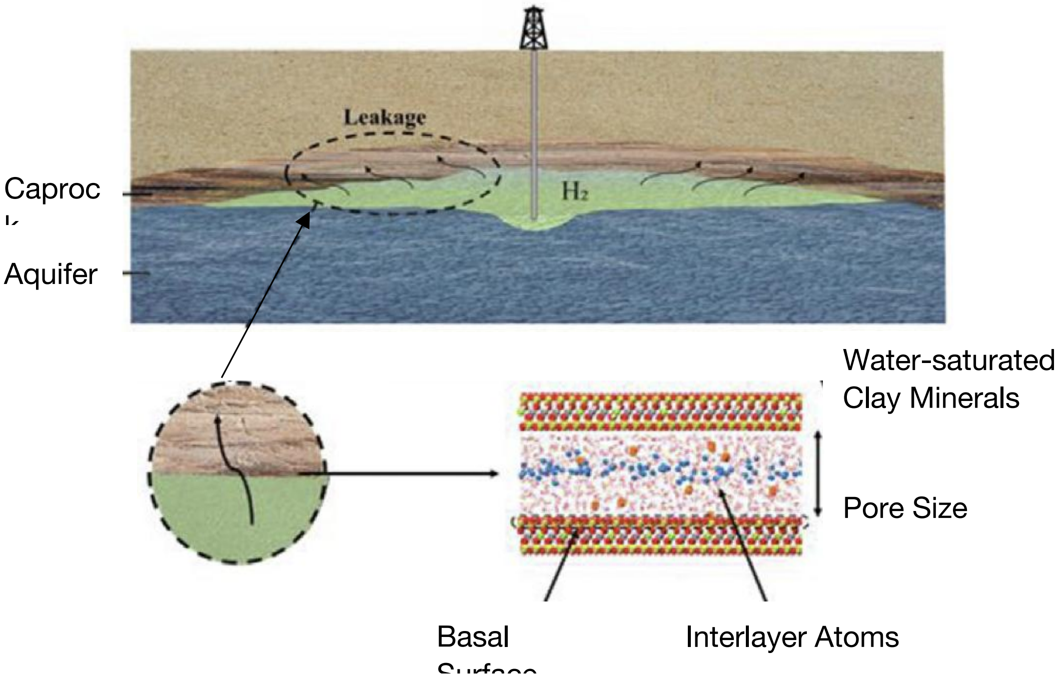


Figure 2. 4 Hydrogen diffusion activity illustration plots. [29]

There are some research proposed that gas diffusion through caprock is not only dependent on primary gas diffusion coefficient, and also caprock mineralogy such as porosity and permeability [28, 30, 31]. It is mainly in the aqueous form which dissolves into brine and flowing away, which is expressed grammatically in figure 2.4 [29, 32]. Within this process, gas-brine-rock interactions need to be considered since aforementioned geochemical interactions such as bacterial sulphate reduction[33], iron reduction[34] and methanogenesis[35]. Because these are all possible factors that alters caprock porosity and permeability. Once caprock mineralogy is changed by hydrogen-brine-rock interactions, caprock sealing capacity from diffusion activity (diffusion depth, diffusion loss) is unknown. There are only some relative literatures studied on gas diffusion loss in carbon sequestration, it shows that pore diffusion of tested rock sample with 6.4% porosity is in order of $2\times10^{-10}$ m$^2$/s which is far less than diffusion of bulk water, which proves $CO_2$ diffusion activity is directly relating to caprock porosity and permeability[36]. However, few paper has precisely addressed hydrogen diffusion depth and diffusion loss in long term storage. Therefore, it is of vital importance to study the relationship between hydrogen diffusion activity and caprock integrity.

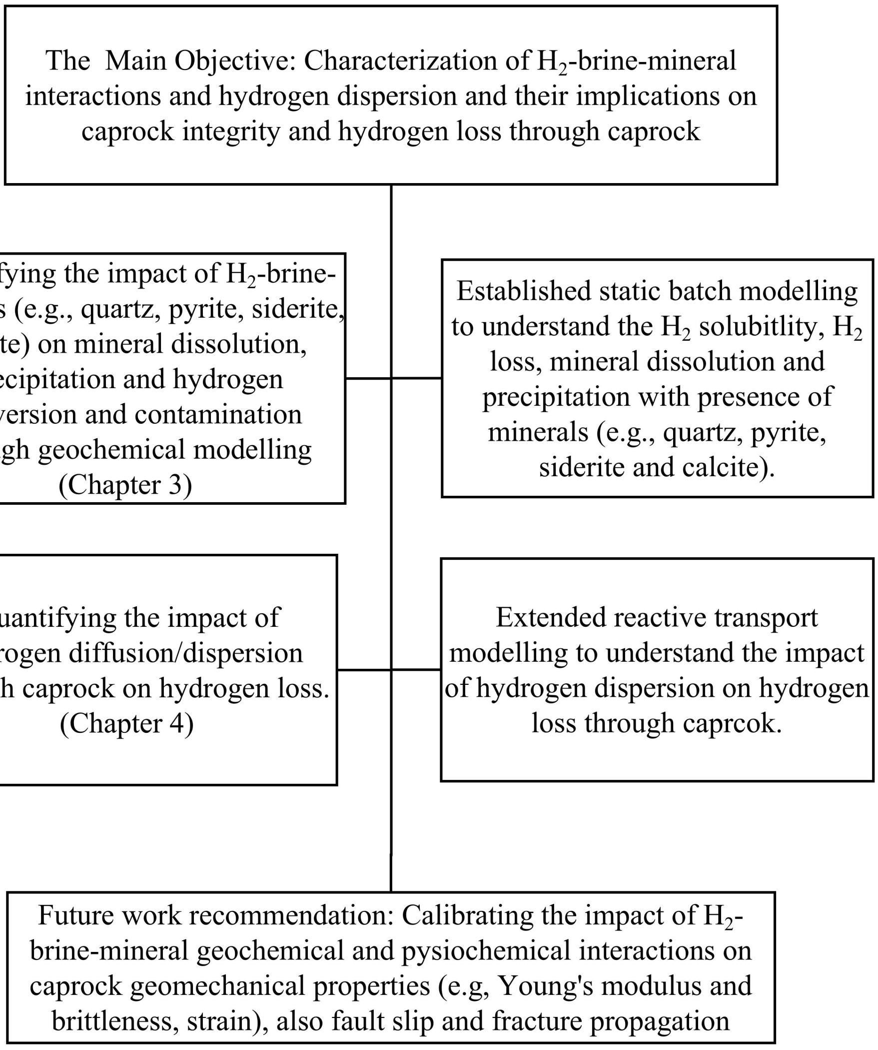
Additionally, pressure and temperature might be the controlling factors on diffusion activity in terms of caprock integrity, since it is reported that geochemical interactions closely dependent on temperature and pressure change and further results to caprock integrity change [18, 32, 37]. For example, in Christina Hemme's report[38], hydrogen diffusion activity was intensified since bacterial sulphate reduction causing pressure elevation. Thus, to improve hydrogen underground storage risk matrix, it is essential to consider the impact of diffusion activity on caprock as a function of temperature and pressure.

# Chapter 3. Research Framework and Methodology

## 3.1 Research Framework

In this section, the whole research framework is to address the main problem that being proposed: how does the hydrogen-brine-mineral interactions and hydrogen dispersion affect caprock integrity in hydrogen subsurface storage. To better address this problem, two sub-objectives are further defined: (1) quantify the impact of H2-brine-minerals (e.g., quartz, calcite, siderite, and pyrite) on mineral dissolution, precipitation and hydrogen conversion and contamination through geochemical modelling. (2) Characterize the impact of hydrogen diffusion/dispersion through caprock on hydrogen loss. To achieve these objectives, both static batch model and reactive transport model were established to cover caprock integrity change in long-term storage and instantaneously. The detailed experiments design and observations are illustrated at following sub-sections. It can be referred to Figure 3.1, which shows the primary framework of this research.

Table 3. 1. The primary research of framework



## 3.2 Methodology

To characterize the impacts and implications of $H_2$-brine-mineral interactions and hydrogen dispersion on caprock integrity and hydrogen loss through caprock, several geochemical modelling were established and categorized into two scenarios. (1) Four static-batch models were designed based on four types of chosen minerals, calcite, quartz, pyrite and siderite. It aims to investigate the caprock integrity change and potential hydrogen loss from $H_2$-brine-mineral geochemical interactions with the assumption of instantaneous reaction state. (2) Eight reactive-transport models were created to study the how hydrogen dispersion activity influent long-term hydrogen storage performance in terms of hydrogen loss and caprock integrity. To simulate as closely as real wellbore condition, it is essential to characterize the pressure and temperature impacts on hydrogen dispersion intensity by subdividing eight models into fixed temperature group and fixed pressure group.

### 3.2.1. Role of redox reaction in caprock integrity

While it has been widely accepted that geochemical reactions play an important role in underground hydrogen storage. It is a complex function of subsurface pressure, temperature, minerals, and brine salinity in terms of caprock integrity. Some studies up to now have descriptively illustrate its possible impacts on hydrogen loss in multi-mineral systems [34, 39, 40]. However, little attention has been paid to quantitatively characterize redox reaction impact of each mineral (quartz, calcite, pyrite and siderite) on caprock integrity in terms of mineral dissolution, porosity, permeability and hydrogen loss. There is evidence showing that 2mg to 8mg dissolved oxygen pre-exists at subsurface depth of 100 meters to 1000 meters[20], this dissolved oxygen is highly possible to involve in geochemical interaction and act as oxidizing agent to intensify redox reaction. Hence, to understand the basic physics behind the redox reaction impact on caprock integrity, the comprehensive geochemical modellings (PHREEQC Version 3) have been developed in terms of four aspects (Chapter 4): (1) Effect of dissolved oxygen concentration and mineral type on hydrogen solubility. (2) Effect of dissolved oxygen concentration and mineral type on pH variation. (3) Effect of dissolved oxygen concentration and mineral type on hydrogen loss and caprock integrity (porosity and permeability).

### 3.2.2. Effect of dissolved oxygen concentration and mineral type on hydrogen solubility.

To calculate hydrogen solubility change in brine with presence of different minerals and oxygen contents, static batch modelling was established to investigate the amount of hydrogen gas dissolves into brine. This process can take place continuously since temperature and pressure keep increasing and more dissolved hydrogen will be consumed in redox reaction. the basic equation that express gas dissolution movement is given below[14]:

$M_i = K_H \frac{\Phi i \ Pi}{\gamma i}$ [14]…………………………………………………………..Equation 1

Where m is the molality in Kg, $K_H$ is the equilibrium constant in mol/Kg and $\gamma$ is the activity coefficient in water (dimensionless), P is the gas partial pressure in atm, Φ is known as fugacity coefficient (dimensionless), which can be calculated by comparing ideal gas law such as Van der Waals Equation[41]:

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2}$$

[41]…………………………………………………………..Equation 2

Where b ($m^3$/mol) is the gas' minimum volume, a (Pa·($m^3$/mol)$^2$) and $\alpha$ (dimensionless) are Van der Waals attraction factors. Peng and Robinson have derives this formula in 1976 to relate these coefficients to the critical pressure in Pa, temperature in kelvin, and the acentric factor of a gas, and providing more accurate gas P-V relationship with fugacity coefficient[41]:

$$\ln(\varphi) = \left(\frac{PV_m}{RT} - 1\right) - \ln\left(\frac{P(V_m - b)}{RT}\right) + \frac{a\alpha}{2.828bRT} \ln\left(\frac{V_m + 2.414b}{V_m - 0.414b}\right)$$

[41]……..Equation 3

### 3.2.3. Effect of dissolved oxygen concentration and mineral type on pH variation

pH is defined as decimal logarithm of the reciprocal of the hydrogen ion activity[36]. It shows the number of free hydrogen ions presenting in solution phase, which indicates redox reaction extent since redox reaction taking place with consuming free hydrogen ions and oxygen. If system showing alkaline condition (pH > 7), it suggests that massive free hydrogen ions in aqueous phase are consumed in the reaction, if the system showing acidic condition (pH < 7), it suggests that excessive free hydrogen ions released into solution, whereas if it is in neutral condition (pH = 7), it indicates that number of $H^+$ and $OH^-$ are in equilibrium state, which is set to be initial value in our case. To observe the redox reaction impact of dissolved oxygen and mineral type on caprock integrity, pH is an important indicator to track reaction state.

$pH = -\log_{10}(\alpha H^+) = \log_{10}\left(\frac{1}{\alpha H^+}\right)$ [36]……………………………………….Equation 4

Where, $\alpha$ is the ion activity constant for hydrogen ions (dimensionless) [36].

### 3.2.4. Effect of dissolved oxygen concentration and mineral type on hydrogen loss and caprock integrity

Caprock integrity change is expressed from porosity and permeability, which can be concluded from mineralogy alteration. While hydrogen injecting into subsurface porous medium, redox reaction between hydrogen, brine and mineral will take place with increasing temperature and pressure, in this case, both dissolved hydrogen and oxygen will react with minerals and results to oxygen, hydrogen and mineral losses. Consequently, caprock mineralogy will be altered if mineral loss occurs, and hence caprock porosity and permeability will be changed and its sealing capacity is affected. PHREEQC is calculating redox reaction in each mineral system based on below geochemical interaction database:

Table 3. 2. Geochemical reaction equations and properties

| No | Reaction Equation | Reaction Constant (logK) | ΔH (kcal) |
|---|---|---|---|
| **1** | $CaCO_3 + 4H^2 = Ca^{2+} + CH_4 + 2OH^- + H_2O$ | -8.48 | -2.297 |
| **2** | $FeS_2 + H_2O = 0.25H^+ + 0.25SO_4^{2-} + Fe^{2+} + 1.75\ HS^-$ | 11.435 | -0.871 |
| **3** | $SiO_2 + 2H_2O = H_4SiO_4$ | -3.98 | 5.990 |
| **4** | $FeCO_3 + 4H_2 = Fe^{2+} + CH_4 + 2OH^- + H_2O$ | -10.89 | -2.480 |

The logic of PHREEQC calculating hydrogen ions and mineral consumption is to count number of moles of species remaining in solution after reaction is finalized, then subtracting from initial number of moles of species[14]. In this case, there are several assumptions need to be made in prior to run the static batch model, for example, system was set to be a closed system with boundary from both inlet and outlet, also hydrogen gas was set to be excessive amount due to massive hydrogen gas volume storing at subsurface in real case.

### 3.2.5. Role of dispersion activity in caprock integrity

Dispersion activity has been proposed as a considerable risk in underground hydrogen storage implementation. There are some papers studied dispersion activity in terms of caprock integrity with descriptive illustration, they proposed that wellbore temperature and pressure might be the dependent factors on diffusion/dispersion activity. However, there is little research conducted to predict the diffusion length and diffusion loss precisely as the function of pressure and temperature, far less attention has been paid to identify implication in hydrogen underground storage. We thus conducted reactive transport modelling to simulate diffusion activity with real wellbore condition and addressed diffusion rate and loss within 30 years of storage time when subsurface pressure and temperature increasing. Three scenarios are covered in this section (Chapter 5). (1) Hydrogen diffusion activity as a function of temperature and storage time at low fixed pressure (100atm). (2) Hydrogen diffusion activity as a function of pressure and storage time at fixed low temperature (25℃). (3) Hydrogen diffusion activity as a function of pressure and storage time at fixed high temperature (70°C).

The reactive transport modelling was established with PHREEQC Version 3 with to simulate diffusion activity. The cell contains water exclusively and uses the pore water diffusion coefficient for calculating the flux. (The effective diffusion coefficient ($D_e$) is for a volume of grains and pores together, and is related to $D_p$ in $m^2/s$ as follows[14]:

$D_e = D_P \varepsilon$ [14]……………………………………………………………………...Equation 5

Where ε is the water-filled porosity (dimensionless), $D_e$ is the effective diffusion coefficient in $m^2/s$, which can be derived from initial diffusion coefficient known as $D_p$ in $m^2/s$ [14].

Also, effective porosity is correlated with temperature change[14]:

$D_w' = (D_w)298 \times \frac{T}{298} \times \frac{\eta_{298}}{\eta_T}$ [14]………………………………………………………..Equation 6

Where η is viscosity of water in cP, T is is simulating temperature in kelvins, $D_w$ is known as initial porosity (dimensionless), and $D_w$’ is temperature correlated porosity (dimensionless) [14].

By counting on dispersion coefficient to obtain overall hydrogen loss and penetration depth:

$\frac{\partial C}{\partial t} =- v\frac{\partial C}{\partial x} + D_L \frac{\partial^2 C}{\partial x^2} - \frac{\partial q}{\partial t}$ [14]…………………………………………………………..Equation 7

Where C is the concentration in water (mol/L), v is the pore water flow velocity in m/s, x is distance in meters, $D_L$ is the dispersion coefficient in $m^2/s$. The term $\frac{\partial C}{\partial t}$ indicates change of species concentration over modelling time in advective transport ($mol/m^3 \cdot s$), $\frac{\partial^2 C}{\partial x^2}$ represents the change of concentration over modelling distance in $mol/L^2$ and $\frac{\partial q}{\partial t}$ is the change in concentration in solid phase due to geochemical reaction ($mol/m^3 \cdot s$)[14].

It is decided to use multi-mineral system to simulate diffusion activity within 30 years of storage time in 100 cells among 100 meters caprock depth. The simulation calculation uses geochemical reaction database at below to assure that hydrogen-brine-mineral interactions will be involved in. The results imply the impact of diffusion activity on hydrogen loss, and hydrogen penetration depth indicates the caprock sealing capacity as the function of storage time, pressure and temperature.

Table 3. 3. Mineral dissolution equations in hydrogen dispersion activity project

| **Minerals** | **Geochemical Reactions** | **$\log K_{298K}$** |
|---|---|---|
| **Illite** | $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2 + 11.2H_2O = 0.6K^+ + 0.25Mg^{2+} + 2.3Al(OH)^{4-} + 3.5H_4SiO_4 + 1.2H^+$ | -40.267 |
| **Quartz** | $SiO_2 + 2\ H_2O = H_4SiO_4$ | -3.98 |
| **Albite** | $NaAlSi_3O_8 + 8H_2O = Na^+ + Al(OH)^{4-} + 3H_4SiO_4$ | -18.002 |
| **Anorthite** | $CaAl_2Si_2O_8 + 8\ H_2O = Ca^{2+} + 2Al(OH)^{4-} + 2H_4SiO_4$ | -19.714 |
| **Chlorite** | $Mg_5Al_2Si_3O_{10}(OH)_8 + 16H^+ = 5Mg^{2+} + 2Al^{3+} + 3H_4SiO_4 + 6H_2O$ | 68.38 |
| **K-feldspar** | $KAlSi_3O_8 + 8H_2O = K^+ + Al(OH)^{4-} + 3H_4SiO_4$ | -20.573 |
| **Pyrite** | $FeS_2 + 2H^+ + 2e^- = Fe^{+2} + 2HS^-$ | -18.479 |
| **Siderite** | $FeCO_3 = Fe^{2+} + CO_3^{2-}$ | -10.89 |

# Chapter 4. Role of Redox Reaction during Hydrogen Underground Storage in Porous Media

## Abstract

Underground Hydrogen Storage (UHS) in porous media appears to be a promising means for large-scale hydrogen storage, underpinning the full-scale of hydrogen supply chain development. Hydrogen-brine-rock interactions play an important role in hydrogen conversion and contamination during hydrogen cycling process. While the redox reaction triggered by injected $H_2$ and pre-existing $O_2$ is unique in UHS compared to other types of gas subsurface storage, few research have been done to understand the role of redox reactions in hydrogen solubility, pH, and fewer works have looked beyond its process on hydrogen conversion and contamination, which may affect the stored $H_2$ purity and storage efficiency. In this context, we examined the redox reactions on hydrogen-brine-minerals (e.g., calcite, siderite, quartz and pyrite) reactions as a function of dissolved oxygen concentration (from 5.5 to 5500 ppm), temperature, and pressure through geochemical modelling using geochemical solver PHREEQC.

Our results showed that increasing dissolved oxygen concentration from 5.5 to 5,500 ppm resulted in negligible impact on hydrogen solubility and pH for all tested minerals. As the sensitive minerals, siderite and calcite can react with $H_2$ through the redox process, leading up to a certain hydrogen loss at the pressure of 20 MPa, respectively. Meanwhile, quartz and pyrite are insensitive minerals to hydrogen, causing less than 0.2% hydrogen loss at the same pressure condition. Our results indicate that the mineral oxidation due to the pre-existing $O_2$ dissolved in formation brine played a negligible role in $H_2$-brine-rock interactions. The results also showed that carbonate minerals such as siderite and calcite may act as electron acceptors, which triggered hydrogen dissociation and thus formed a strong

reduction environment based on PHREEQC geochemical database. This process likely causes measurable hydrogen loss associated with abiotic geochemical reactions for the lifetime of the underground hydrogen storage operation. Taken together, we suggest that clean sandstone reservoirs will significantly reduce the hydrogen conversion and contamination during underground hydrogen storage from abiotic geochemical perspective.

## 4.1 Introduction

Hydrogen energy appears to play an important role in energy transition, and is one of the most promising solutions for decarbonization of fossil fuel intensive industries[1, 3]. To underpin the energy transition, the development of hydrogen economy supply chain is of vital importance, including hydrogen production[1, 42] , transmission[2], transportation[37, 43] and storage[2, 44]. There are a few ways to store hydrogen. For example, hydrogen can be stored in the form of compressed gas[24, 44], liquids through high pressure tanks[45, 46], and solids through physio-chemical adsorption[47, 48]. However, these surface hydrogen storage facilities have limited storage capacity with magnitude of only MW and the relatively short storage period which usually ranges from hours to days[44]. To meet the global hydrogen energy demand in the scale of GW and TW and longer storage period (weeks to months), large-scale hydrogen storage is paramount to achieve the energy transition[28, 49-51]. Meanwhile, underground hydrogen storage (UHS) has been proposed as a promising means to storage hydrogen in a cost-effective and scalable manner[2, 52-54]. However, current studies are far from enough to understand the processes and risks taking place during UHS, including $H_2$ conversion and contamination, storage integrity, storage performance, etc[52, 55-57]. Therefore, it is urgent and necessary to quantify and manage the potential risks associated with hydrogen storage due to geochemical reactions[58, 59].

There are a few areas related to geochemical reactions for the evaluation of the feasibility of underground hydrogen storage at subsurface, such as caprock sealing capacity[60], caprock and wellbore integrity[56, 61-63], hydrogen transport in reservoirs[28, 64-66] and hydrogen contamination[67-70]. Caprock sealing capacity and wellbore stability are dependent on pre-existing geological environment and petrophysical properties[5, 71-74]. Once the pre-existing geological features (e.g., porosity, permeability, and geological stress) are altered by hydrogen-brine-rock interactions, the overall sealing capacity of caprock and integrity of wellbore would be affected[75-78]. This process may initiate hydrogen loss through migration pathways in wellbore and (or) caprock, which may compromise the underground hydrogen storage projects.

Hydrogen-brine-rock interactions are also associated with reservoir wettability, which plays an important role in hydrogen transport in reservoirs. In general, most of underground depleted reservoirs are stated in water-wet conditions regardless of mineral compositions, temperature and pressure[56, 79]. However, the stored hydrogen and the distribution of injected/pre-existing cushion gas can affect the multiphase flow regime by altering relative permeability and capillary pressure due to wettability variation[2, 80-83]. Previous studies have characterized the wettability of sandstone reservoirs, with both static and dynamic modelling to test whether wettability is changed by gas composition ($H_2$, $CO_2$ and $CH_4$)[84, 85], pressure[79] and temperature[15, 86] by using microfluidics[87, 88], tilted plate[63, 81], core flooding[89, 90] and captive-bubble cell methods[91, 92]. Although published work[86, 93] has confirmed that wettability has insignificant dependency on pressure temperature and salinity, there is still lack of wettability study with consideration of geochemical reactions, especially the redox reaction caused by $H_2$. The redox reactions between minerals and stored hydrogen may not only lead to $H_2$ conversion and contamination, but also reservoir performance and long-term storage integrity.

Furthermore, the *in-situ* dissolved hydrogen, either pre-existed in the formation brine or pumped from surface during $H_2$ cycling process, may react with certain types of minerals and leads to extra hydrogen conversion and contamination[2, 3, 58, 62, 94]. For example, the dissolved carbonates minerals can react with hydrogen and cause methane generation due to the redox reaction[94]. Bo et al.,[95] performed geochemical modelling to assess the $H_2$ loss and the degree of mineral dissolution as the result of hydrogen-brine-rock interactions in sandstone reservoirs. They reported that the main reason of hydrogen loss in the tested sandstone reservoirs is because of the presence of calcite. Besides, some $SO_4^{2-}$ associated minerals such as anhydrite can also trigger redox reaction and form $H_2S$, which further reduces the purity of stored hydrogen[96, 97].

While a few more geochemical modelling works[58, 98, 99] have been recently conducted to characterize the risks and uncertainties regarding hydrogen loss and hydrogen-brine-rock interactions, the question of the role of redox reaction on hydrogen conversion and contamination during UHS remains to be answered. One of the concerns stems from the impact of dissolved oxygen (DO) on fluid-rock interactions thus $H_2$ conversion and contamination. The concentration of dissolved oxygen in formation brine commonly ranges from 2 to 8 mg per litre[100]. While $O_2$ would act as an electron acceptor to oxidize ions at low valence state, the stored $H_2$ can act as electron donor to reduce ions at high valence state. However, the role of existing $O_2$ and injected $H_2$ on mineral dissolution and gas composition change as result of redox reaction, particularly at reservoir temperature and pressure conditions, is still incomplete. Therefore, this study aimed to determine whether the redox reaction would trigger significant hydrogen conversion and contamination with various minerals under various pressure and temperature conditions.

## 4.2 Methodology

Given that the concentration of oxygen as oxidizing agent at subsurface ranges from 2 to 8 milligram per litre or ppm at the depth of 100 to 1000 meters[100], in this study, we used 5.5 ppm as the average dissolved oxygen content. Besides, to reveal the extreme impact of redox reaction on hydrogen loss, a wider range of dissolved oxygen contents (5.5-5500 ppm) was also considered in a static thermodynamic model. Furthermore, four mineral types were selected in this study, including calcite, quartz, pyrite, and siderite, which represent in carbonate reservoirs and sandstone reservoirs with carbonate cementation/infill materials. We did not examine clay minerals (e.g., illite, smectite, chlorite and kaolinite) because these minerals are insensitive to hydrogen especially in redox reactions although these minerals are still associated redox reactions through acid and base reactions[101, 102].

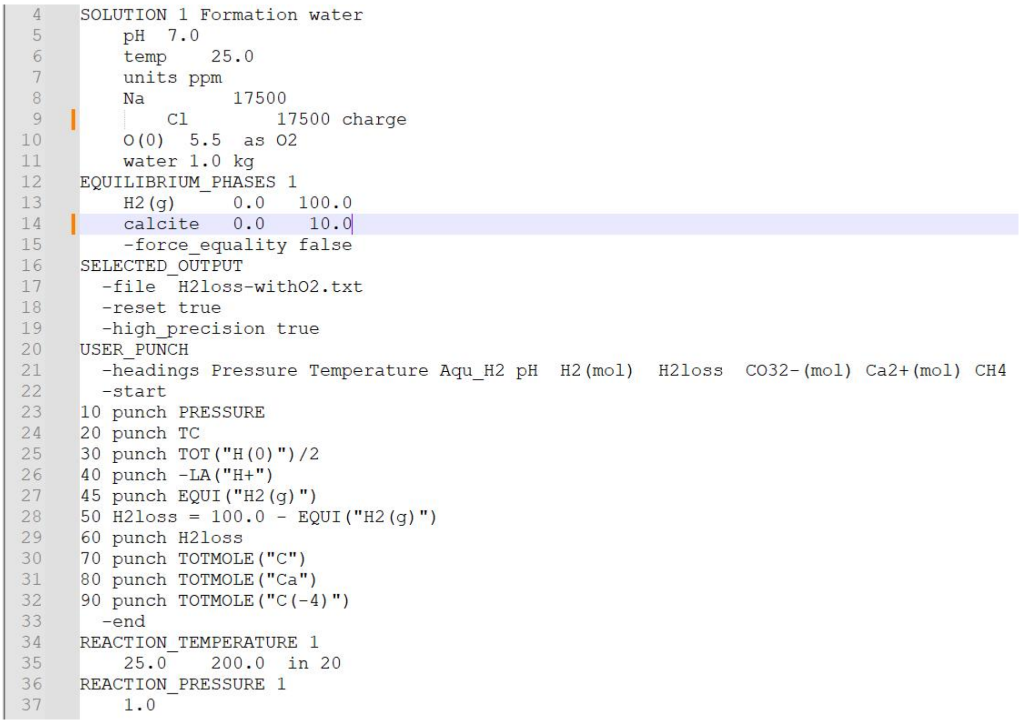
Table 4. 1. Simulation conditions & reactant description in static modelling

| $H_2$ Gas | Mineral Type | Mineral Contents | Connate Water Salinity | Temperature | Pressure | Residual Connate Water | DO Concentration |
|---|---|---|---|---|---|---|---|
| 100 moles | Calcite<br>Quartz<br>Siderite<br>Pyrite | 10 moles | 35000 ppm NaCl | 25℃ - 200℃ | 1 – 1000 atm | 1kg | 5.5ppm,<br>55ppm,<br>550ppm,<br>5500ppm |

Table 4. 2. Geochemical Reaction Table

| No | Reaction Equation | Reaction Constant (logK) | ΔH (kcal) |
|---|---|---|---|
| **1** | $CaCO_3 + 4H^2 = Ca^{2+} + CH_4 + 2OH^- + H_2O$ | -8.48 | -2.297 |
| **2** | $FeS_2 + H_2O = 0.25H^+ + 0.25SO_4^{2-} + Fe^{2+} + 1.75\ HS^-$ | 11.435 | -0.871 |
| **3** | $SiO_2 + 2H_2O = H_4SiO_4$ | -3.98 | 5.990 |
| **4** | $FeCO_3 + 4H_2 = Fe^{2+} + CH_4 + 2OH^- + H_2O$ | -10.89 | -2.480 |

Table 4. 3. PHREEQC tool interface setup



```
SOLUTION 1 Formation water
    pH  7.0
    temp    25.0
    units ppm
    Na        17500
        Cl        17500 charge
    O(0)  5.5  as O2
    water 1.0 kg
EQUILIBRIUM_PHASES 1
    H2(g)     0.0   100.0
    calcite   0.0    10.0
    -force_equality false
SELECTED_OUTPUT
  -file  H2loss-withO2.txt
  -reset true
  -high_precision true
USER_PUNCH
  -headings Pressure Temperature Aqu_H2 pH  H2(mol)  H2loss  CO32-(mol) Ca2+(mol) CH4
  -start
10 punch PRESSURE
20 punch TC
30 punch TOT("H(0)")/2
40 punch -LA("H+")
45 punch EQUI("H2(g)")
50 H2loss = 100.0 - EQUI("H2(g)")
60 punch H2loss
70 punch TOTMOLE("C")
80 punch TOTMOLE("Ca")
90 punch TOTMOLE("C(-4)")
  -end
REACTION_TEMPERATURE 1
    25.0    200.0  in 20
REACTION_PRESSURE 1
    1.0
```

To cover wide range of geological formation for possible underground hydrogen storage, the geochemical modelling in this study was carried out with pressure from 1 to 1000 atm, temperature from 25 to 200°C (Table 4.1). As an example in Table 4.3, it is showing that calcite system setup for 5.5ppm dissolved oxygen content in brine. By changing the mineral and oxygen contents, we aim to understand the impact of redox reaction during UHS with presence of $O_2$ on i) solubility of hydrogen, ii) pH and pE, and iii) hydrogen loss and methane production in brine with various dissolved oxygen concentration for different mineral (calcite, quartz, pyrite, and calcite). Solubility of hydrogen is an indicator to show the ability of brine dissolving hydrogen gas[56, 95]. The pH variation together with pE would reflect the degree of hydrogen loss and extent of reduction environment[95]. Lastly, hydrogen loss and methane generation provides the direct evidence of the intensity of redox reaction in this study[56, 103].

## 4.3 Results and Discussion

### 4.3.1 Effect of dissolved oxygen concentration and mineral type on hydrogen solubility

Increasing oxygen concentration from 5.5 to 5,500 ppm did not increase hydrogen solubility regardless of mineral type. For example, the hydrogen solubility maps as a function of pressure and temperature were all overlapped for all examined mineral (Figures 4.1 to 4.5). This also indicates that excess amount of injected hydrogen tends to form a strong reduction condition, which suppresses oxidation process.

Clearly, Figures 4.1 to 4.5 show that hydrogen-brine-minerals geochemical reactions indeed affected the hydrogen solubility in the system at a given pressure and temperature although the solubility of hydrogen overall was minor. Quartz and pyrite showed a similar hydrogen solubility map as a function of pressure and temperature (Figures 4.1 and 4.2). For example, at a given pressure, hydrogen solubility increased with temperature. At a given temperature, hydrogen solubility increased with pressure. This is because that molecules activity would be intensified with the increase of pressure and temperature[104] and thus more hydrogen gas can dissolve into brine. This pattern is in line with the hydrogen solubility in brine without minerals (Figure 4.3). The same trend was also observed from the geochemical modelling from Bo et al, [56]. It is worth noting that Bo et al., [56] show a much lower hydrogen solubility compared to Figures 4.1 to 4.3. This is mainly because partial pressure of hydrogen in this study was set as same as the system pressure. In Bo et al., [56] work, the partial pressure was set as a constant with increasing system pressure.

Quartz gave the same hydrogen solubility profile with a pure brine system (Figure 4.1 and Figure 4.3). This is because hydrogen-brine-quartz system triggered minor mineral dissolution and any gas production to occupy gas solubility in brine[101, 105]. It is worth noting that quartz solubility experiment was operated at 800℃ and 10,000 bars by equilibrating two natural gem-quality crystals with water, showing minor quartz dissolution in brine [106]. Therefore, hydrogen solubility increment in quartz system is not related to geochemical process with quartz rather the physical process as a function of temperature and pressure increasing. Similarly, pyrite also gave the same trend of minor mineral dissolution impacts on hydrogen solubility profile as function of pressure and temperature (Figure 4.3). Here we only modelled single mineral system with limited dissolved oxygen concentration at anaerobic conditions at subsurface, which may not trigger hydrogen-brine-pyrite geochemical interactions. However, the impact of hydrogen-brine-pyrite interactions needs to be further investigated in multi-mineral system, especially with co-existing carbonates minerals [66, 75, 107, 108]. Our results show that hydrogen interactions with quartz and pyrite alone have negligible impact on hydrogen solubility, suggesting that quartz-rich sandstone reservoirs would have low risks in hydrogen conversion and contamination from geochemical reactions perspective.

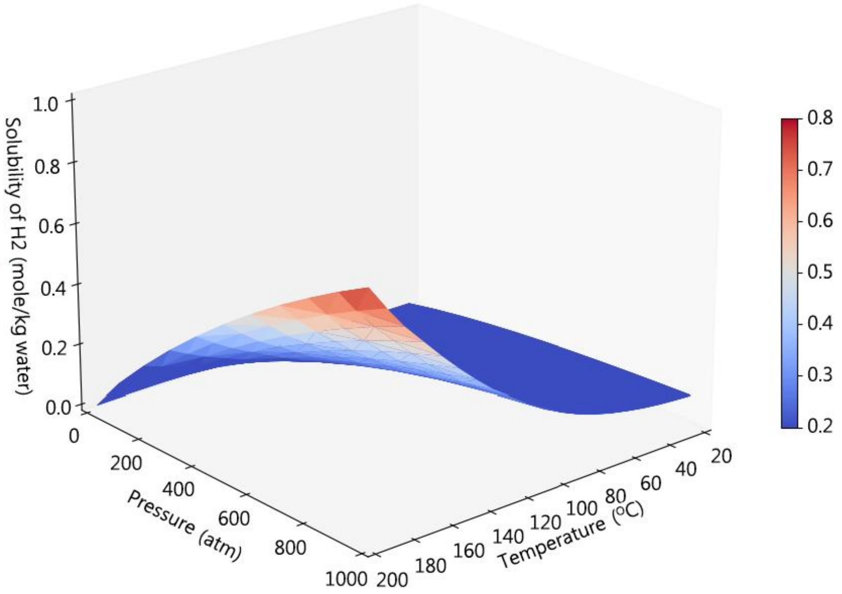


Figure 4. 1. $H_2$ solubility as function of temperature and pressure in the presence of 35000 ppm brine and 10 moles of quartz

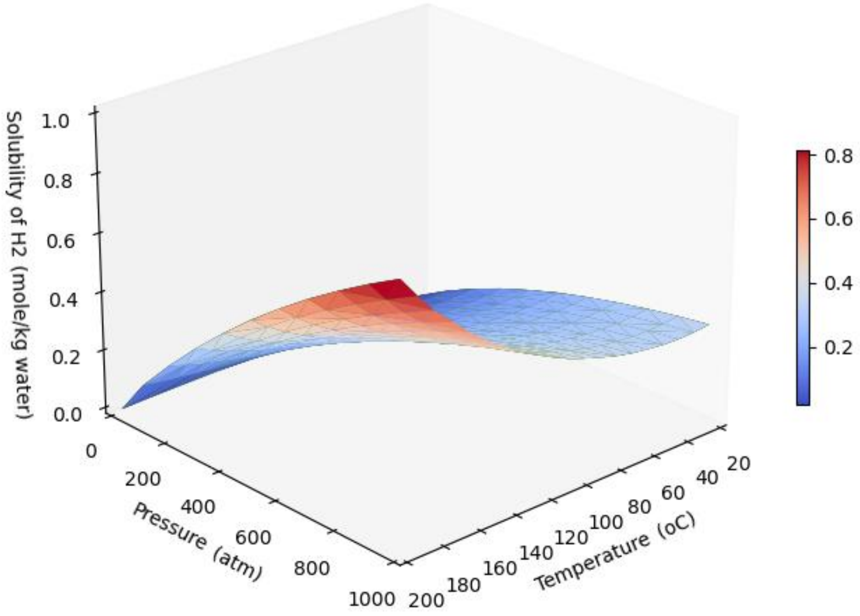


Figure 4. 2. $H_2$ solubility as function of temperature and pressure in the presence of 35000 ppm brine and 10 moles of pyrite

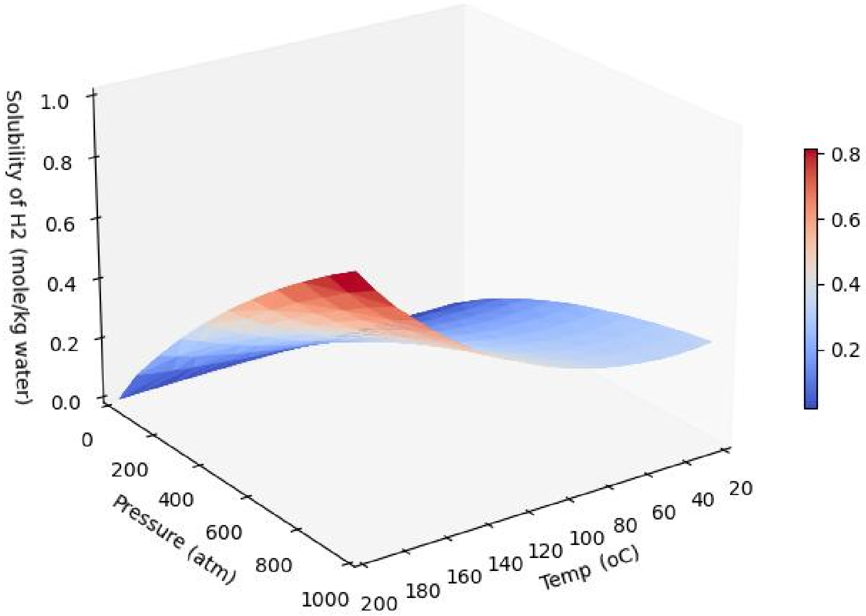


Figure 4. 3. $H_2$ solubility as function of temperature and pressure in 35000 ppm pure brine system

Unlike quartz and pyrite, calcite minerals gave parabolic trend (U-shape) in hydrogen solubility as a function of pressure and temperature. For example, at a given pressure, hydrogen solubility initially decreased till temperature up to 120℃. Afterwards, hydrogen solubility increased with temperature. Similarly, at a given temperature, increasing pressure increased hydrogen solubility with pressure up to 100MPa. It is worth noting that calcite leads to the lowest $H_2$ solubility compared with all rest of the examined minerals. This is due to the fact that calcite-brine-hydrogen redox reactions produce $CH_4$[109] based on the geochemical data base used in this study, which occupies partial brine solubility, hence causing overall lower solubility of hydrogen in calcite-brine system compared to other minerals. In contrast, siderite did not show significant hydrogen solubility initially although siderite also belongs to carbonate-based mineral. This is mainly because $FeCO_3$ is relatively stable than $CaCO_3$ with limited $CH_4$ generation[92, 110, 111]. For example, the equilibrium constant (LogK) for siderite dissolution process is -0.19, but it is 1.84 for calcite dissolution. Our results suggest that hydrogen solubility in brines is not only a function of salinity, pressure, and temperature, but also associated with $H_2$-brine-mineral geochemical reactions. This may generate new gases in the system through redox reactions. Our results also explains why Bo[56] observed lower solubility of $H_2$ in brine-calcite system compared with clay minerals.

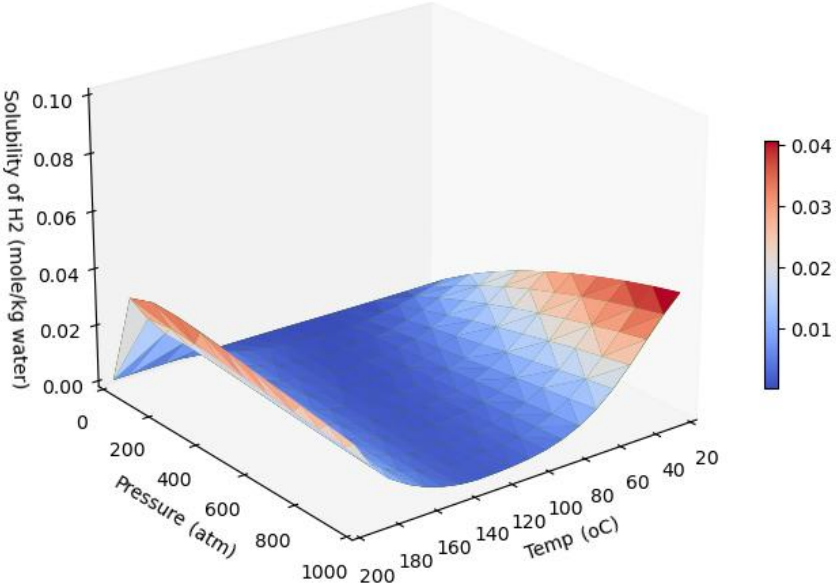


Figure 4. 4. $H_2$ solubility as function of temperature and pressure in the presence of 35000 ppm brine and 10 moles of calcite

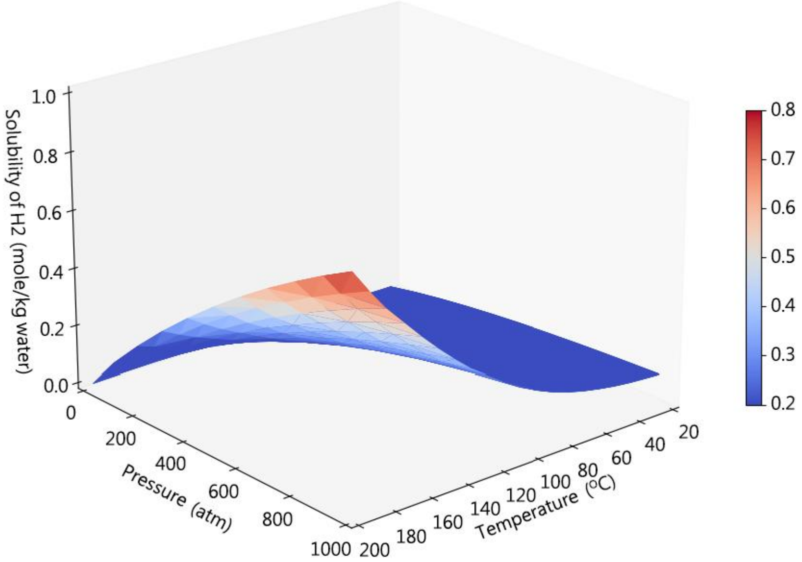


Figure 4. 5. $H_2$ solubility as function of temperature and pressure in the presence of 35000 ppm brine and 10 moles of siderite

### 4.3.2 Effect of dissolved oxygen concentration and mineral type on pH variation

The presence of oxygen played a negligible role in hydrogen-brine-mineral systems' pH regardless of the oxygen concentrations tested in this study, indicating that dissolved $O_2$ concentration tested in this study has negligible impact on $H^+$ consumption. For example, the pH for all five cases had almost no changes, which can be seen from the overlapped 3D graphs regardless of oxygen concentrations and minerals (Figure 4.6 to 4.10). The negligible pH variation implies that hydrogen ions concentration of all cases remains constant regardless of dissolved oxygen concentration. Our results suggest that the pre-existing $O_2$ in formation brine during UHS have negligible impact on hydrogen conversion and contamination.

However, mineral type has significant impact on pH with presence of $H_2$ as the function of pressure and temperature. For example, sulphate minerals, quartz and pure brine system alone showed neutral environment with pH from 6.0 to 7.0 in the examined pressure and temperature (Figures 4.6 to 4.8). In addition, quartz-brine system and brine system along showed almost the same range of pH with pressure and temperature. However, carbonated minerals, such as calcite and siderite-hydrogen-brine systems gave a strong base condition with pH from 8.0 to 13.0 with pressure and temperature (Figures 4.9 and 4.10).

Quartz-brine alone with hydrogen showed a slightly acidic condition with pH blow 7 as a function of pressure and temperature. This is mainly because increasing temperature facilitates water dissociation, which generates hydronium ($H_3O^+$) and hydroxide ($OH^-$)[56, 111], leading to a lower pH value (Figure 4.6 and Figure 4.8). Similarly, pyrite system behaves same pH profile as quartz but with slightly higher pH in high temperature level. This is because at low temperature, the pyrite solubility in brine is considered as insoluble in a single mineral system. When temperature is greater than 100°C, pyrite reduction caused by hydrogen would be slightly accelerated[66, 71, 112, 113], resulting to a minor pH increment compared to quartz.

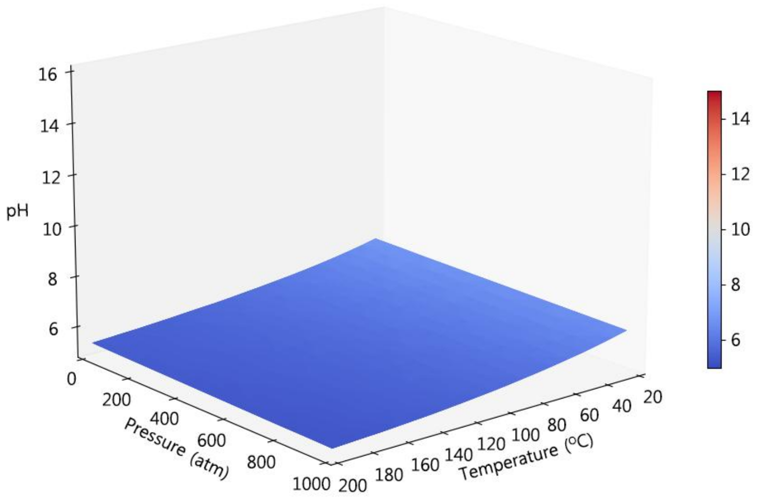


Figure 4. 6. pH variation as function of temperature and pressure in the presence of 35000 ppm brine and 10 moles of quartz

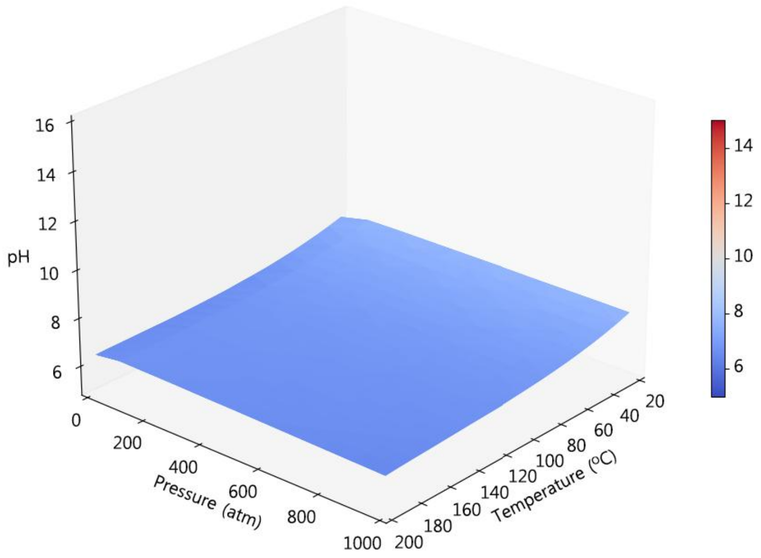


Figure 4. 7. pH variation as function of temperature and pressure in the presence of 35000 ppm brine and 10 moles of pyrite

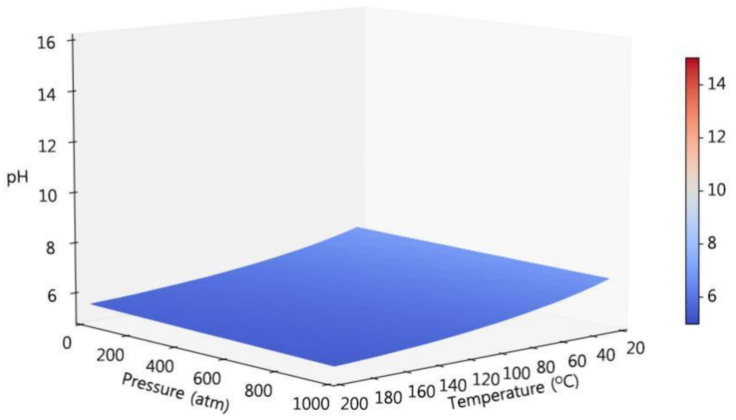


Figure 4. 8. pH variation as function of temperature and pressure in 35000 ppm NaCl brine

$H_2$-brine-carbonate reactions trigger a highly basic condition. For example, $H_2$-brine carbonate systems gave pH from 9 to 14, and $H_2$-brine-siderite gave pH from 9 to 11, whereas $H_2$-brine-calcite system gave pH from 9.5 to 14. The basic condition is mainly due to the redox reactions, which can be explained by Reaction 1 in Table 4.2.

Temperature plays an important role in $H_2$-brine-carbonate redox reactions and thus pH. For example, for calcite, pH increased from 9.5 to 14 with temperature from 20℃ to 200℃. Similarly, for siderite, pH increased from 9 to 11 when temperature increased from 20℃ to 200℃. The trend of the pH variation with temperature is consistent with Zeng et al., [62] who modelled calcite dissolution and hydrogen loss due to the fluid-rock interaction over 500 years during UHS in Majiagou carbonate formation. However, our simulation gave a great 1 to 2 unit higher than the prediction made by Zeng et al., [62]. This is mainly because we performed batch equilibrium modelling with the assumption of excess amount of hydrogen and brine, which gave results at infinite time scale. While in real cases, it is unlikely to reach such high pH value due to limited storage time and large hydrogen gas volume. Given that Reaction 1 and 4 are exothermic reactions (Table 4.2), decreasing temperature facilitates the reactions, increasing $OH^-$. This explains why pH increased with lowering temperature at a given pressure. This also accounts for the lower pH increase of siderite system compared to calcite system due to the lower equilibrium constant for siderite-hydrogen redox reactions. Apart from the redox reactions, mineral dissolution process may also affect the redox reactions hence pH. For example, siderite dissolution rate increased with increasing temperature, thus more hydrogen ions consumed and expressed alkaline pH value. Although the two processes contribute to the pH increase with lowering temperature, the dominant process with hydrogen abiotic geochemical reactions remains open for discussion.

Reaction consumes more $H^+$ to produce carbanions and methane with increasing temperature. This process causes disequilibrium of $H^+$ and $OH^-$ and hence leading to higher pH state[9, 29]. Furthermore, mineral dissolution rate is also a controlling factor in pH variation. For instance, calcite may consume the significant amount of $H^+$ [15, 95], thus triggering a more alkaline condition (pH=15). Whereas siderite dissolution rate is relative lower and hence produces less carbanions and results to less alkaline status[66, 114]. Besides, for siderite-brine system, previous research shows that FeO might be generated as the result of siderite decomposition[111, 112], which can be further reduced by hydrogen to solid iron. However, we did not observe the generation of solid iron as final products in the simulation. The possible reason is that decomposition of siderite to FeO may only take place at extremely high temperature condition[111, 112, 114-116], which is far beyond the temperature limit in our simulation.

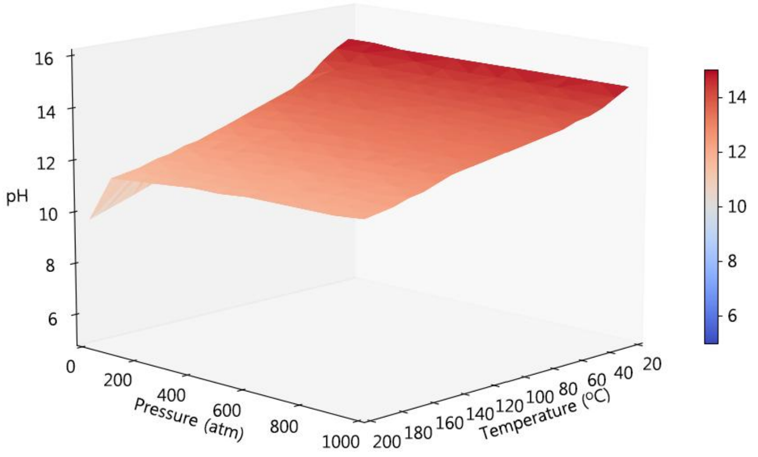


Figure 4. 9. pH variation as function of temperature and pressure in the presence of 35000 ppm brine and 10 moles of calcite

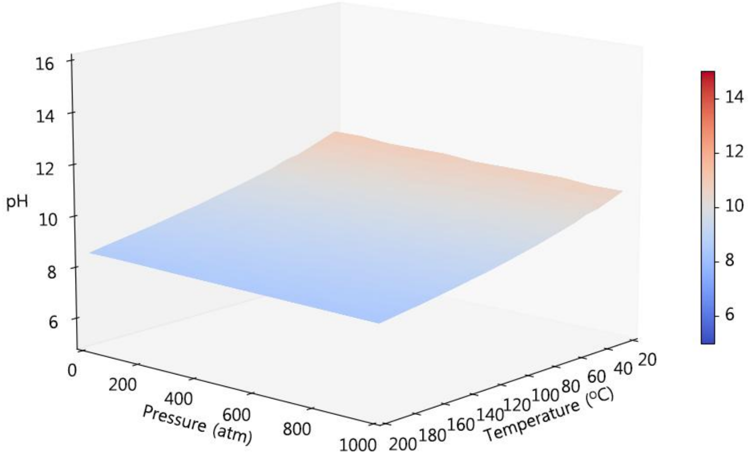


Figure 4. 10. pH variation as function of temperature and pressure in the presence of 35000 ppm brine and 10 moles of siderite

### 4.3.3 Effect of dissolved oxygen concentration and mineral type on hydrogen loss

Dissolved oxygen concentration from 5.5 to 5500 ppm played a minor role in $H_2$-brine-mineral . For instance, results showed that hydrogen loss as a function of pressure and temperature generated less than 0.2% difference from 5.5 ppm dissolved oxygen to 5500 ppm dissolved oxygen, although the hydrogen loss profile from each oxygen concentration is not absolutely overlapping (Figures 4.11 to 4.15). Thus, our results suggest that subsurface porous media with a certain level of oxygen concentration promotes a strong reducing environment due to excessive presence of hydrogen.

However, mineral types has considerable impact on hydrogen loss with presence of $H_2$ as the function of pressure and temperature. Different minerals showed hydrogen loss from 0.1% to 41% at given temperature and pressure for a given hydrogen-mineral system. For instance, quartz and pyrite (Figure 4.11 and 4.12) exhibited less than 1% hydrogen loss, which was almost the same as hydrogen loss profile in pure brine system (Figure 4.13). Unlikely, carbonates mineral systems caused a strikingly higher hydrogen loss. For example, calcite initially maintained 40% hydrogen loss at low pressure and temperature zone, and decreased with increasing temperature but increased with pressure increasing. Whereas siderite system generated 40% hydrogen loss initially and kept increasing to 41% with both temperature and pressure increasing.

Temperature change in quartz and pyrite system showed negligible impacts on hydrogen loss. For example, at high temperature, hydrogen loss in both quartz and pyrite system slightly increased 0.15% with increasing pressure, whereas at low temperature, pressure change had no impact on hydrogen loss. The results indicated that within the simulated condition, temperature contributed negligible impacts to hydrogen loss resulting from redox reaction in both pyrite and quartz systems, which was in line with literature[111, 117]. The main reason was due to the limited mineral dissolution equilibrium constant in brine. Quartz is considered as almost insoluble in brine which contributes no impact to hydrogen loss from mineral effect. All hydrogen loss increment from quartz model was resulting from the hydrogen solubility in brine rather the mineral dissolution process. Without considering microbial activities and methane generation, no direct pyrite reductive dissolution in single mineral system has been observed, whereas slight oxidative dissolution of pyrite is discovered in neutral and alkaline condition without oxygen presenting[66, 75, 112, 118, 119]. This oxidation dissolution was observed to be intensified in strong acidic condition with the presence of sufficient $O_2$[107, 120]. The product of $Fe^{3+}$ from oxidation dissolution process can be further reduced to $Fe^{2+}$ and zero-valent iron with $H_2$ buffering[108, 121]. This finding shows that $Fe^{3+}$ formation from pyrite oxidative dissolution requires sufficient oxygen contents, which is invalid in normal subsurface anerobic condition, unless the multi-mineral system provides an initial acidic environment to support $Fe^{2+}$ oxidised to $Fe^{3+}$ with oxygen presenting. Hence, redox reaction of pyrite system almost showed an invisible hydrogen loss increment based on the modelling.

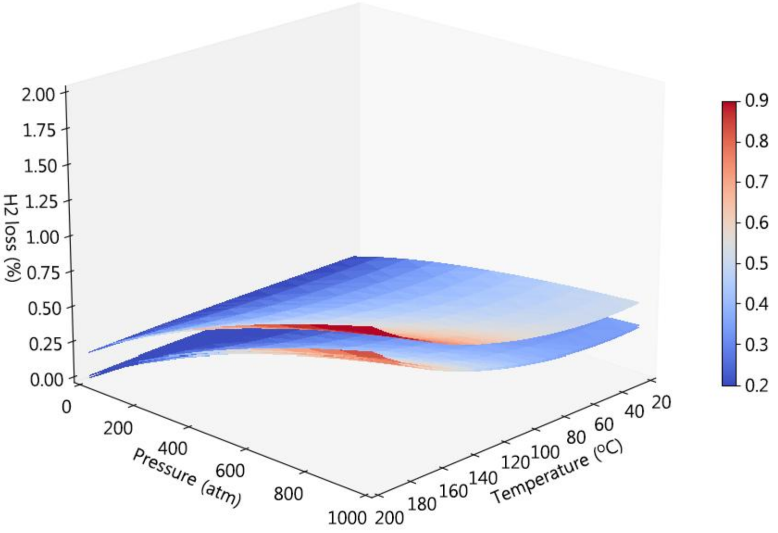


Figure 4. 11. $H_2$ loss as function of temperature and pressure in the presence of 35000 ppm brine and 10 moles of quartz

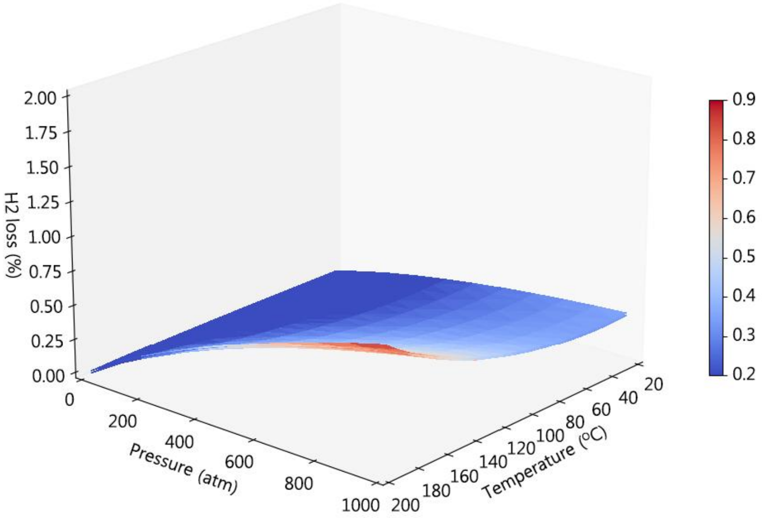


Figure 4. 12. $H_2$ loss as function of temperature and pressure in the presence of 35000 ppm brine and 10 moles of pyrite

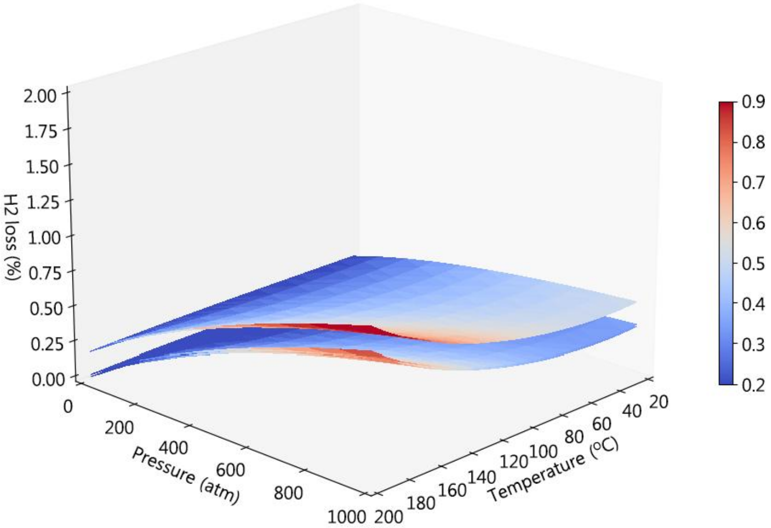


Figure 4. 13. $H_2$ loss as function of temperature and pressure in 35000 ppm NaCl brine

Temperature plays an important role in $H_2$-brine-carbonate redox reaction and thus causing significant hydrogen loss. For example, hydrogen loss in calcite system decreased from 40% to almost zero with temperature increased from 20℃ to 200℃, and hydrogen loss in siderite system increased from 40% to 41% with temperatrure increased from 20℃ to 200℃. The trend of hydrogen loss profile is in line with Bo[95] who modelled hydrogen loss in minerals-brine system. However, our results is 20% higher than prediction made by Bo et al., [95, 122]. This is mainly due to the partial pressure assumption difference, we have assumed that hydrogen partial pressure increased with reaction pressure increasing, whereas Bo et al., [95, 122] assumed hydrogen partial pressure remains constantly while reaction pressure increasing. The results from simulation from this study is consistent with Zeng et al., [62] and Bo et al., [95, 121, 122], showing hydrogen conditioned carbonates dissolution and methanogenesis. Within the carbonates redox reaction process, both calcite and siderite dissolved in brine and produced $HCO_3^-$. It is likely to further consume hydrogen ions to support methane generation process. However, this $CH_4$ production in calcite system will be gradually suppressed due to calcite dissolution rate decreasing with increasing temperature [123, 124], and hence results in decrement tendency in hydrogen loss. The siderite system generated incremental hydrogen loss profile with increasing temperature and pressure due to the fact that its dissolution rate increases with increasing temperature and pressure [72]. In addition, FeO and/or $FeOH_3$ production from siderite decomposition possibly triggers further Fe ions reduction by consuming $H^+$ and precipitates solid iron eventually[114, 125, 126]. However, it is observed that no solid Fe precipitates presents in final solution, because $Fe^{2+}$ is relatively stable in most conditions. Hydrolysis of $Fe^{2+}$ and further reduction reaction may only occur at extremely high temperature conditions (temperature above 200 °C) with sufficient oxygen presenting, which is beyond our tested range.

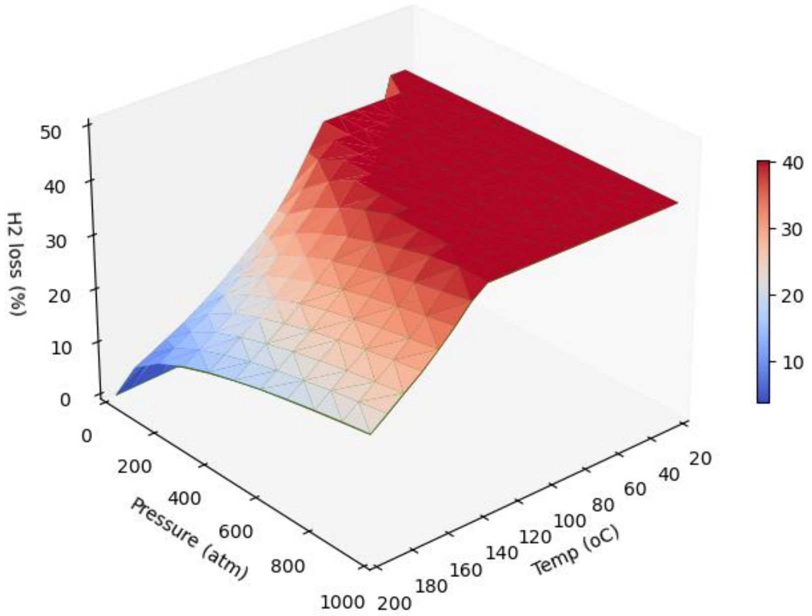


Figure 4. 14. $H_2$ loss as function of temperature and pressure in the presence of 35000 ppm brine and 10 moles of calcite

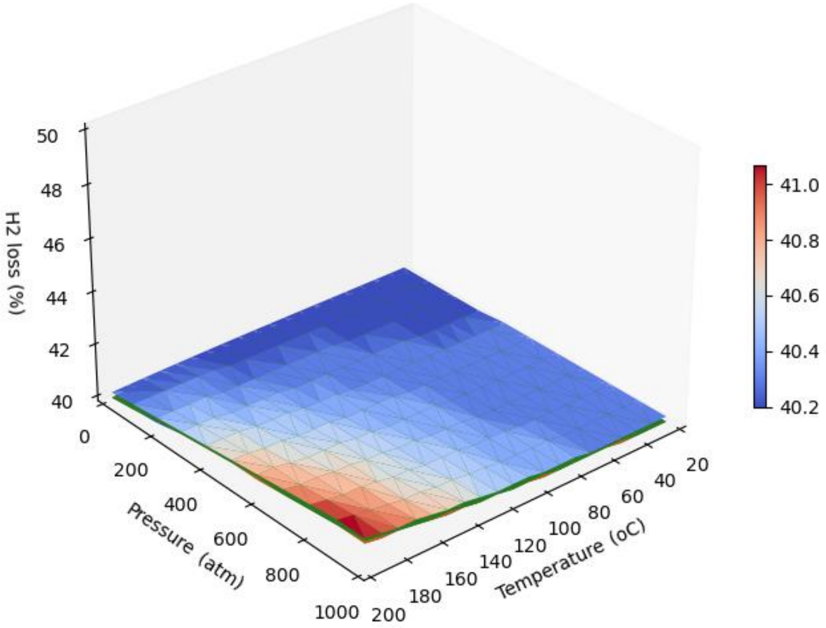


Figure 4. 15. $H_2$ loss as function of temperature and pressure in the presence of 35000 ppm brine and 10 moles of siderite

### 4.3.4 Effect of Carbonate Dissolution on Hydrogen Loss and Methanogenesis

Carbonates dissolution rate played an important role in hydrogen loss and methanogenesis. The tendency of carbonates dissolution and further methanogenesis is represented by pE parameter, which indicates the negative logarithm of ionic concentration in redox equilibrium state. The more negative value of pE is, the stronger reduction environment would be formed and more intense redox reaction takes place[9]. Siderite behaved with a negative pE up to -9.5 with increasing pressure but less negative with increasing temperature. Calcite showed more negative tendency pE of -10.5 with increasing pressure but less negative with increasing temperature.

The pE observation indicated that strong reducing environment efficiently intensifying redox reaction process and leading to an alkaline condition due to $H^+$ consumption from its further methanogenesis reaction[16, 111, 127]. The main reason of causing pE of both calcite and siderite more negative with increasing pressure and less negative with temperature, is due to the fact that increasing temperature leads to a reduction of dissolved hydrogen ions, whereas increasing pressure increases molecules packing and thus intensifying reduction process[107, 124].

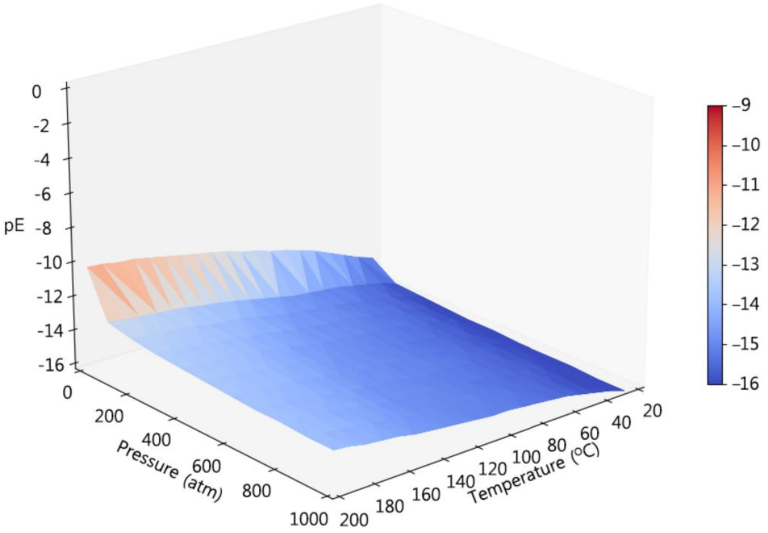


Figure 4. 16. pE variation from 10 moles of calcite and 35000ppm brine system

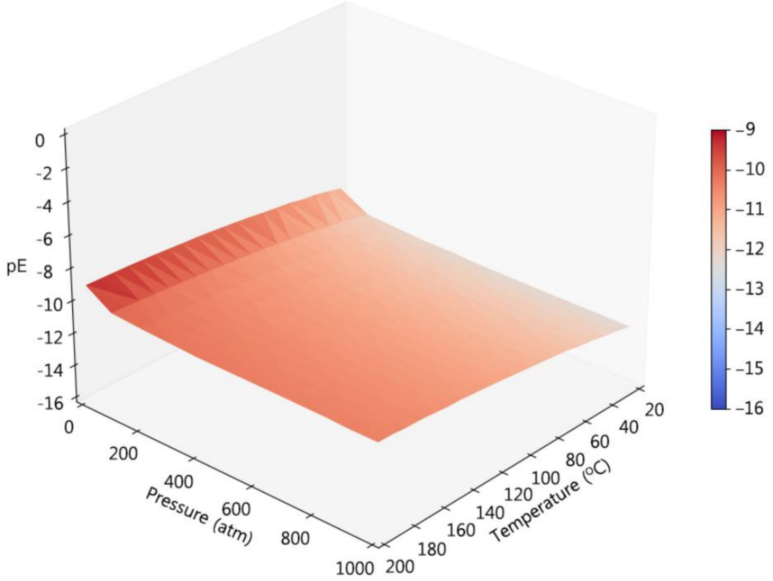


Figure 4. 17. pE variation from 10 moles of siderite and 35000ppm brine system

Temperature played an important role in hydrogen loss and methanogenesis activity. For example, $CH_4$ generation in calcite system showed constantly 10 moles with temperature increase from 20℃ to 100℃, and started to decrease to almost zero with increasing temperature from 100℃ to 200℃, whereas siderite system showed constantly 10 moles of methane production with temprature and pressure. This finding is in line with Hemme et al., [119] who simulated methanogenesis activity through reactive transport modelling and showing that significant amount of $HCO_3^-$ from carbamates dissolution and pre-existing $CO_2$ have been converted to $CH_4$.

The amount of methane generation in carbonate-brine systems is associated with mineral dissolution equilibrium constant and temperature[128]. For example, calcite dissolution process gives enthalpy of ΔH(-25.7) [129] as an exothermic reaction. When temperature increasing, $HCO_3^-$ production was restrained, causing a reduction in methane generation and hydrogen loss. Siderite has a more negative enthalpy ($\Delta H$ -32) [129], which requires an even a higher temperature to suppress this abiotic reactions, inhibiting $CH_4$ production compared to calcite-hydrogen system.

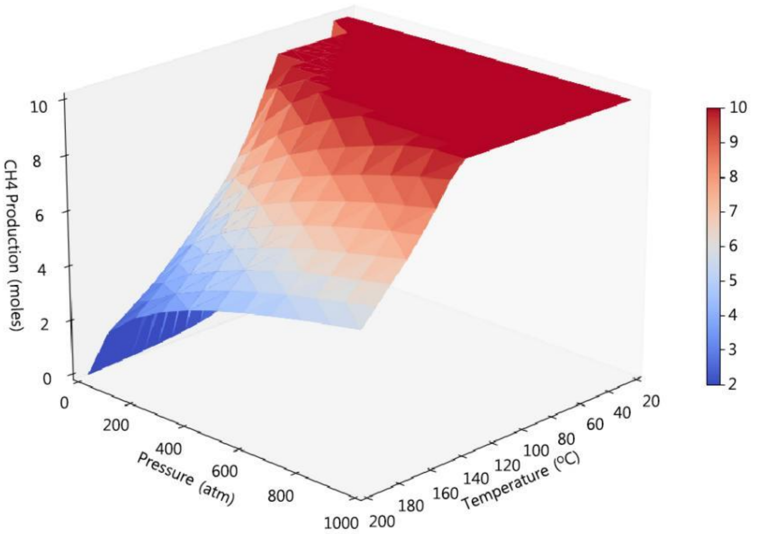


Figure 4. 18. $CH_4$ production from 10 moles of calcite and 35000ppm brine system

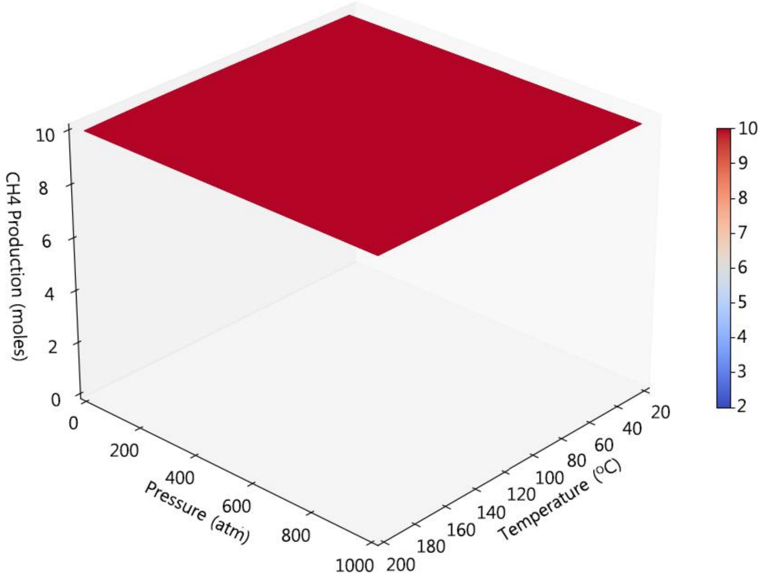


Figure 4. 19. $CH_4$ production from 10 moles of siderite and 35000ppm brine system

Table 4. 4 Comparison table of $H_2$ solubility, pH, $H_2$ loss, pE and $CH_4$ production in each mineral system

| **Minerals** | **Temperature Range (℃)** | **Pressure Range (atm)** | **$H_2$ Solubility in Brine (mol/kg water)** | **pH** | **$H_2$ Loss (%)** | **pE** | **$CH_4$ Production (moles)** |
|---|---|---|---|---|---|---|---|
| Quartz | 20 - 200 | 1 – 1000 | 0.1 – 0.8 | 5.5 – 8 | 0.2 – 0.9 | -- | -- |
| Pyrite | 20 - 200 | 1 – 1000 | 0.1 – 0.8 | 6 – 8 | 0.2 – 0.9 | -- | -- |
| Calcite | 20 - 200 | 1 – 1000 | 0.01 – 0.04 | 10 – 15 | 10 – 40 | -10 to -16 | 2 – 10 |
| Siderite | 20 - 200 | 1 – 1000 | 0.1 – 0.8 | 8 – 12 | 40 – 41 | -9 to -12 | 10 |
| Pure brine | 20 - 200 | 1 – 1000 | 0.1 – 0.8 | 5.5 – 8 | 0.2 – 0.9 | -- | -- |

It is worth noting that recent experimental measurements on the interactions of $H_2$-brine-limestones (mainly calcite and dolomite) system imply that carbonate minerals seem non-reactive to aqueous hydrogen at realistic reservoir temperature and pressure conditions [98, 130]. These experimental results are not in line with the results from geochemical modelling as aforementioned, where considerable fractions of calcite and siderite would dissolve due to the redox reactions with $H_2$. The main reason behind the inconsistency is tentatively attributed to the invalidation of the database for geochemical modelling when $H_2$ is participated in the system. In the current *phreeqc.dat*, the methanogenesis process is defined as $CO_3^{2-} + 10\ H^+ + 8\ e^- = CH_4 + 3\ H_2O$ ($-\log K = 41.071$, $-\Delta H = -61.039$ kcal). The conversion from $CO_2$ ($CO_3^{2-}$) to $CH_4$ requires extra electrons. For current geochemical modelling on $H_2$-brine-rock interactions, the source of electrons is assumed to be the dissociation of aqueous $H_2$ ($H_2 \rightarrow 2H^+ + 2e-$). However, since $H_2$ is such geochemical-stable molecule, its dissociation at reservoir temperature and pressure conditions should be extremely weak. Therefore, much care should be taken when using this reaction to simulate the $H_2$-brine-carbonate geochemical reactions. The equilibrium constant needs to be constrained or even the reaction might be completely inactivated to match the experimental results [131, 132]. However, it is worth noting that if microbial activities are considered in the simulation, it is expected to observe the methanogenesis since microbes can provide extra e- and act as catalyst to accelerate the e- transfer from donor to acceptor [133]. However, the microbial related $H_2$ conversion is commonly considered as kinetic-controlled rather equilibrium-controlled process, so that other methods (for example, the Monod Equation) may be applied to accurately depict microbial activities, which is beyond the scope of this work.

## 4.4 Conclusions and Implications

Our geochemical modelling shows that increasing concentration of dissolved oxygen from 5.5ppm to 5500ppm resulted in minor (0.2%) hydrogen loss in all systems in this study, even 5500ppm DO is still insufficient to support oxidation reaction. $Fe^{2+}$ minerals such as pyrite are unlikely to be involved in redox reaction under 20 °C -200 °C temperature and 100atm-1000atm pressure due to a lack of oxygen to promote iron oxidative dissolution to $Fe^{3+}$. Given that most of underground condition was classified as anaerobic environment, the presence of dissolved oxygen on hydrogen conversion and contamination is negligible.

While temperature and pressure have a minor impact on hydrogen loss for quartz and pyrite regardless of DO concentrations, temperature and pressure indeed play an important role in hydrogen-brine-carbonate systems, triggering a certain hydrogen loss based on the current PHREEQC thermodynamics database in particular at temperature below 100°C. Hydrogen-brine-carbonate systems lead to redox reactions triggered by mineral dissolution, which is confirmed by pH increase and strongly negative pE. While thermodynamics modelling shows a certain amount of hydrogen loss during the infinite time process (upper limit) with presence of carbonate-based minerals, we expect that hydrogen loss will be significantly reduced with kinetics involved with and without DO. Taken together, we suggest that clean sandstone reservoirs will significantly reduce the hydrogen conversion and contamination during underground hydrogen storage from abiotic geochemical perspective.

# Chapter 5. Impact of Hydrogen Dispersion through Caprock on Hydrogen Loss and Its Implications for Underground Storage

## Abstract

Hydrogen is a promising energy carrier for transitioning from traditional fossil fuels to renewables. Underground hydrogen storage (UHS) in depleted hydrocarbon reservoirs plays a crucial role in supporting the full-scale and long-term hydrogen economy supply chain. However, concerns have been raised regarding the caprock seal capacity during the hydrogen storage process, as hydrogen is the smallest molecule and may diffuse away from the caprock when temperature and pressure increase. Therefore, it is essential to assess the potential risks associated with hydrogen diffusion during the hydrogen storage process. In this study, we conducted geochemical modelling using PHREEQC (Version 3.0) software to investigate hydrogen loss and diffusion distance resulting from the diffusion process through caprock as a function of pressure and temperature.

To examine the impact of pressure and temperature on hydrogen diffusion, we established three models, each focusing on one variable. The results obtained from PHREEQC were converted into pseudo 3D graphs using Spyder, which revealed that both temperature and pressure affect hydrogen diffusion and loss differently. While an increase in temperature can lead to an instantaneous hydrogen diffusive loss of $1.3\times10^{-9}$ moles, an increase in pressure can only slow down the diffusion rate. Additionally, neither temperature nor pressure significantly contributes to diffusion depth variation within tested conditions, which is less than 60cm depth from the surface. Therefore, the $1.3\times10^{-9}$ moles of aqueous diffusion hydrogen loss and 60cm diffusion penetration depth are considered negligible in the underground hydrogen storage risk matrix. Our findings provide a screening tool for mitigating the risks associated with hydrogen loss through caprock during the hydrogen diffusion process.

## 5.1 Introduction

The development of hydrogen as a clean energy source has garnered considerable attention and support worldwide[2], with over 50 countries endorsing the Lofoten Declaration to promote the transition from fossil fuels to hydrogen[1, 3, 66]. The Australian government has also committed \$275.5 million to develop four hydrogen hubs, with a goal to incorporate up to 50% hydrogen in the national energy mix by 2050[16, 56, 134]. However, hydrogen's volumetric inferior calorific value of 3kWh/$m^3$ is the lowest among fuels compared with other fuels, although the mass energy density is the highest (33.3 kWh/kg) [94, 135, 136]. Therefore, its large storage space requirement has raised concerns about its feasibility as a long-term energy carrier. To overcome this issue, large-scale hydrogen storage systems are being developed, with underground porous mediums such as salt caverns, depleted hydrocarbon reservoirs, and aquifers being the most viable options for safe long-term storage[2, 53, 137, 138].

However, hydrogen loss during storage remains a significant challenge, with several factors contributing to this issue, including caprock geochemical interactions, sealing capacity, and diffusion loss [2, 139-141]. Hydrogen's high diffusion coefficient makes it vulnerable to escape through caprock formations, resulting in significant hydrogen loss[2, 95, 142, 143]. Heinemann[52] also stated that this type of hydrogen loss is possibly in the form of aqueous phase and it requires to further improved simulation modelling and gain deeper understanding of hydrogen escaping depth and hydrogen loss amount in long-term storage project. Thus, understanding the factors that influence hydrogen loss and developing strategies to mitigate it is crucial for the success of underground hydrogen storage.

In this context, evaluating aqueous hydrogen loss due to diffusion is a critical step in determining the feasibility of subsurface hydrogen storage. The sealing capacity of caprock, such as mineral composition and thickness, is a critical factor that needs to be taken into account[5, 12], with previous studies indicating that carbonate-rich reservoirs have resulted in significant hydrogen loss. Therefore, in this study, carbonates-poor reservoirs are selected for caprock composition data to determine the caprock thickness requirement to prevent hydrogen loss[54, 95, 144]. Furthermore, the impacts of diffusion on hydrogen loss over long-term storage (from months to decades) need to be examined, with both periodical hydrogen loss and final hydrogen loss across the entire storage time evaluated[145]. Additionally, reservoir temperature and pressure are also two significant controlling factors, with higher temperatures and pressures leading to more hydrogen loss due to increased hydrogen activity and hydrogen diffusion activity, respectively[9, 10, 139, 146].

To address these challenges, this report uses the PHREEQC [14] kinetic simulation model to identify the hydrogen loss from caprock diffusion processes as a function of storage time, pressure, and temperature. The study also illustrates how hydrogen loss varies with increasing caprock depth and effectively identifies the caprock thickness requirement to prevent significant hydrogen loss during long-term underground hydrogen storage under increasing pressure and temperature. These findings will aid in developing strategies to mitigate hydrogen loss and establish a viable underground hydrogen storage system, thus supporting the transition to a cleaner energy future.

## 5.2 Methodology

A one-dimensional (1D) geochemical transport modelling has been performed to examine the process of hydrogen advection, diffusion, and dispersion on hydrogen loss, and gain a deeper understanding of the hydrogen diffusion process through caprock as a function of temperature, pressure and storage time. All geochemical modelling process were established by PHREEQC (Version 3.0)[14] and the results were plotted in pseudo 3D graphs by Spyder. The minerology composition of this simulation modelling is from Gassum reservoirs[147], which is selected as poor carbonates reservoir. Because there are a few hydrogens subsurface storage reports have stated that carbonates minerals can cause significant hydrogen loss from geochemical reaction[90, 92, 95], which indicates that carbonates-rich reservoirs will be excluded from UHS site selection.

To generally predict the hydrogen loss from diffusion process, three different temperature level and three pressure level were chosen to cover wide range of reservoir condition, which are listed at Table 5.2. Thereinto, the reference scenario was decided to be 100atm and 25°C, to be compared with other cases to observe hydrogen diffusion process impacts as a function of temperature and pressure. A combination of qualitative and quantitative methods was used in this investigation from the following three aspects.

i. Hydrogen aqueous diffusion loss as a function of temperature and storage time when pressure is fixed at 100atm.
ii. Hydrogen aqueous diffusion loss as a function of pressure and storage time when temperature is fixed in low level (25°C))
iii. Hydrogen aqueous diffusion loss as a function of pressure and storage time when temperature is fixed in high level (70°C)

Hydrogen aqueous diffusion loss plots are expected to express the amount of stored hydrogen escaped through caprock and indicating accurate penetration depth at different time spot. The master transport model was primarily designed with 100 cells among the 100cm caprock. There are only initial 5 cells occupied with $H_2$ gas. The results are expected to show the diffusion depth after 5 cells at given storage time (30 years). Furthermore, the average shale porosity was taken from literature resources 4.04%[148], hence, 20.2L pore volume were estimated and thus, total volume of brine is 10.1L when Sw = 50%, both dispersivity and diffusion coefficient are collected from PHREEQC database which are $1 \times 10^{-5}$ and $5 \times 10^{-9}$ respectively. Apart from reservoir physical properties, the given caprock composition at Table 5.1 is required to convert from weight percentage to number of moles, and brine data were taken from report written by Andre and Azaroual[149], and the volume of brine was set to be 0.202kg. As an example in Table 5.4 reference case with temperature of 25 ℃ and pressure of 100 atm, inputting aforementioned parameters in initial model and gradually increasing temperature and pressure to compare the impact of hydrogen dispersion activity on hydrogen loss and caprock integrity as the function of temperature and pressure.

Table 5. 1. Gassum Reservoir Mineralogy[147]

| **Minerals** | **Weight%** |
|---|---|

| | |
|---|---|
| Illite | 60 |
| Quartz | 14 |
| Albite | 6 |
| Anorthite | 3 |
| Chlorite | 5 |
| K-feldspar | 4 |
| Pyrite | 4 |
| Siderite | 3 |
| Anatase | 1 |

Table 5. 2. Temperature and pressure condition in all cases

| **Case No.** | **Temperature ℃** | **Pressure (atm)** |
|---|---|---|
| Reference Case 1 | 25 | 100 |
| Case 2 | 50 | 100 |
| Case 3 | 80 | 100 |
| Case 4 | 25 | 200 |
| Case 5 | 25 | 300 |
| Case 6 | 70 | 100 |
| Case 7 | 70 | 200 |
| Case 8 | 70 | 300 |

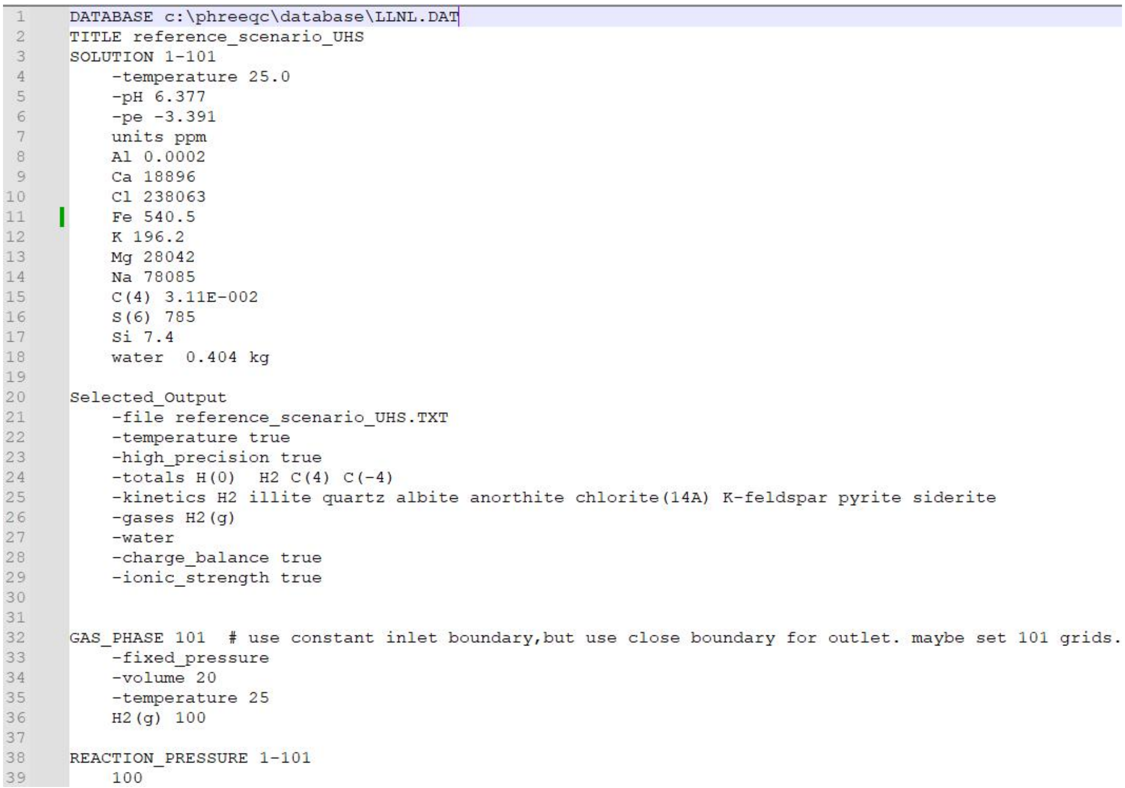
Table 5. 3. Brine Composition[147]

| **Elements** | **Composition (mg/L)** |
|---|---|
| Na | 78085 |
| K | 196.2 |
| Ca | 18896 |
| Mg | 28042 |
| Fe | 540.5 |
| Cl | 238063 |
| Al | 0.0002 |
| Si | 7.4 |
| S | 785 |

Table 5. 4. Geochemical Reactions[56]

| Minerals | Geochemical Reactions | $LogK_{298K}$ |
|---|---|---|
| **Illite** | $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2 + 11.2H_2O = 0.6K^+ + 0.25Mg^{2+} + 2.3Al(OH)^{4-} + 3.5H_4SiO_4 + 1.2H^+$ | -40.267 |
| **Quartz** | $SiO_2 + 2\ H_2O = H_4SiO_4$ | -3.98 |
| **Albite** | $NaAlSi_3O_8 + 8H_2O = Na^+ + Al(OH)^{4-} + 3H_4SiO_4$ | -18.002 |
| **Anorthite** | $CaAl_2Si_2O_8 + 8\ H_2O = Ca^{2+} + 2Al(OH)^{4-} + 2H_4SiO_4$ | -19.714 |
| **Chlorite** | $Mg_5Al_2Si_3O_{10}(OH)_8 + 16H^+ = 5Mg^{2+} + 2Al^{3+} + 3H_4SiO_4 + 6H_2O$ | 68.38 |
| **K-feldspar** | $KAlSi_3O_8 + 8H_2O = K^+ + Al(OH)^{4-} + 3H_4SiO_4$ | -20.573 |
| **Pyrite** | $FeS_2 + 2H^+ + 2e^- = Fe^{+2} + 2HS^-$ | -18.479 |
| **Siderite** | $FeCO_3 = Fe^{2+} + CO_3^{2-}$ | -10.89 |

Table 5. 5 PHREEQC tool interface of initial condition setup with temperature of 25 ℃ and pressure of 100 atm



```
DATABASE c:\phreeqc\database\LLNL.DAT
TITLE reference_scenario_UHS
SOLUTION 1-101
    -temperature 25.0
    -pH 6.377
    -pe -3.391
    units ppm
    Al 0.0002
    Ca 18896
    Cl 238063
    Fe 540.5
    K 196.2
    Mg 28042
    Na 78085
    C(4) 3.11E-002
    S(6) 785
    Si 7.4
    water  0.404 kg

Selected_Output
    -file reference_scenario_UHS.TXT
    -temperature true
    -high_precision true
    -totals H(0)  H2 C(4) C(-4)
    -kinetics H2 illite quartz albite anorthite chlorite(14A) K-feldspar pyrite siderite
    -gases H2(g)
    -water
    -charge_balance true
    -ionic_strength true


GAS_PHASE 101  # use constant inlet boundary,but use close boundary for outlet. maybe set 101 grids.
    -fixed_pressure
    -volume 20
    -temperature 25
    H2(g) 100

REACTION_PRESSURE 1-101
    100
```

The logic of PHREEQC modelling diffusion process is based on aforementioned Equation 7, where $D_L$ in $m^2/s$ is the dispersion coefficient. The term $\frac{\partial C}{\partial t}$ in mol/L/s indicates change of species concentration over modelling time in advective transport, $\frac{\partial^2 C}{\partial x^2}$ in represents the change of concentration over modelling distance in dispersive transport and $\frac{\partial q}{\partial t}$ is the change in concentration in solid phase due to geochemical reaction[14].

$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D_L\frac{\partial^2 C}{\partial x^2} - \frac{\partial q}{\partial t}$ [14]……………………………………………………….....Equation 7

Furthermore, the kinetic model was used to express the continuity of diffusion process, and all kinetic constants of minerals were selected from PHREEQC manual book[14]. Additionally, there is an assumption in this model, which is sealed system, it means not considering the underground water flowing condition and capillary pressure threshold is not exceeded, also it is not considering micro-fractures in this project. Additionally, there is also a constraint to use PHREEQC to model diffusion process, which is incapable of simulating multiphase flow in caprock pores, hence, $H_2$ loss from diffusion process in this report is only representative as the aqueous hydrogen loss in single phase flow.

## 5.3 Results and Discussion

### 5.3.1 Temperature variation with fixed pressure (100 atm)

By analysing output data files using pseudo 3D plots, we can observe that temperature elevation significantly impacts the hydrogen diffusive loss profile, and this impact is only evident in the first 10 years and the first 40cm depth. For example, as temperature increasing from 25 ℃ to 80 ℃, the hydrogen diffusion loss increased $1.3 \times 10^{-9}$ moles within first 10 years and 40cm depth, then the system reached equilibrium after 40cm depth. The diffusion behaviour can be explained by Fick's Law[28, 31, 32], which states that diffusion occurs when there is a concentration difference between two ends, and it will keep diffusing until the concentration of two ends is similar. Meanwhile, higher temperature provides higher molecular activity to intensified hydrogen diffusion movement and caused instantly higher hydrogen loss.[150, 151]. Also, this finding is consistent with Bo[95] stated, as temperature increasing, more hydrogen gas is dissolving into brine as the form of aqueous phase, which increases hydrogen concentration difference between underground and surface. This also can be proved by pH variation plots in Figure 5.4, where the pH level increased as the temperature increases due to more aqueous $H^+$ diffusing through caprock. Hence, higher reservoir temperatures lead to hydrogen concentration and molecular activity increment in the aqueous phase and thus temporarily increase diffusive hydrogen loss[137, 152, 153]. However, the highest instant hydrogen loss in case 3(T=80℃) is only $1.3 \times 10^{-9}$ moles, which is still considered as negligible in UHS risk assessment.

Another noteworthy phenomenon is that as the temperature increases, storage time plays an important role in the hydrogen diffusion process. For instance, in figure 5.3 with temperature of 80℃ , the whole diffusion process takes less than 5 years to reach diffusive equilibrium, and in the case of 50℃, it requires 10 years, whereas, in the case of 25℃, it requires almost 30 years. This occurs because as the temperature increases, hydrogen concentration in brine also increases, leading to an increment in molecule free-path length and further causing free-motion velocity to speed up while slowing down the number of molecule collisions, thereby increasing the diffusion rate.[52, 82]. Therefore, based on the negligible diffusion hydrogen loss (1.3 × $10^{-9}$ moles) at 80℃, the higher temperature is, the shorter time required to reach to diffusion equilibrium.

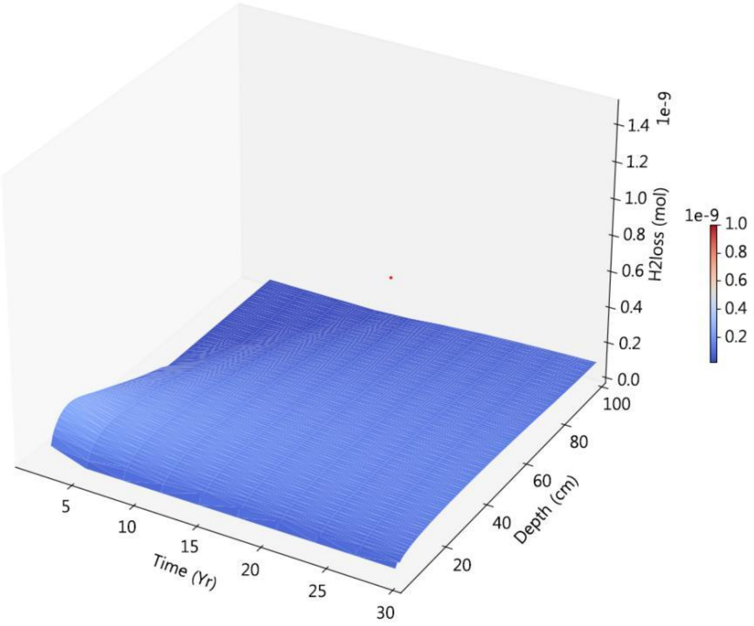


Figure 5. 1. Reference Case1-when T=25℃ and P=100atm

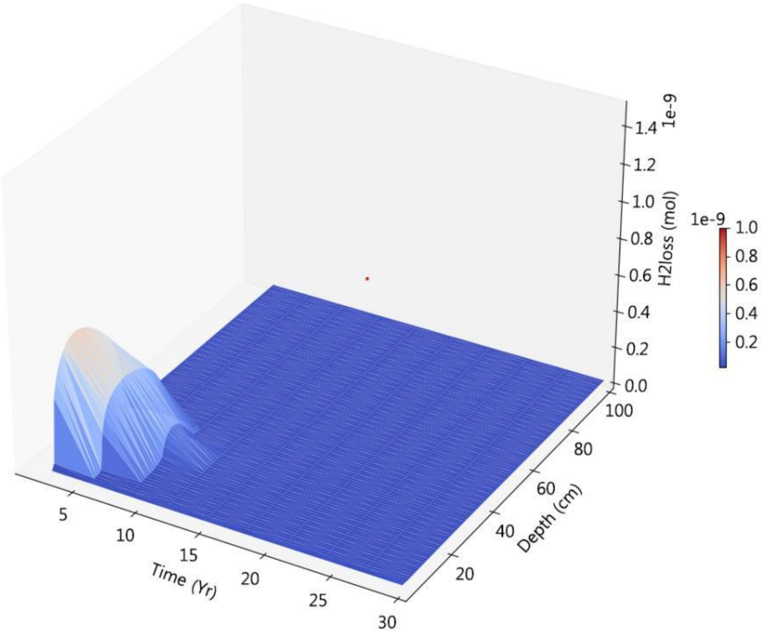


Figure 5. 2. Case2-$H_2$ loss when T=50℃ and P=100atm

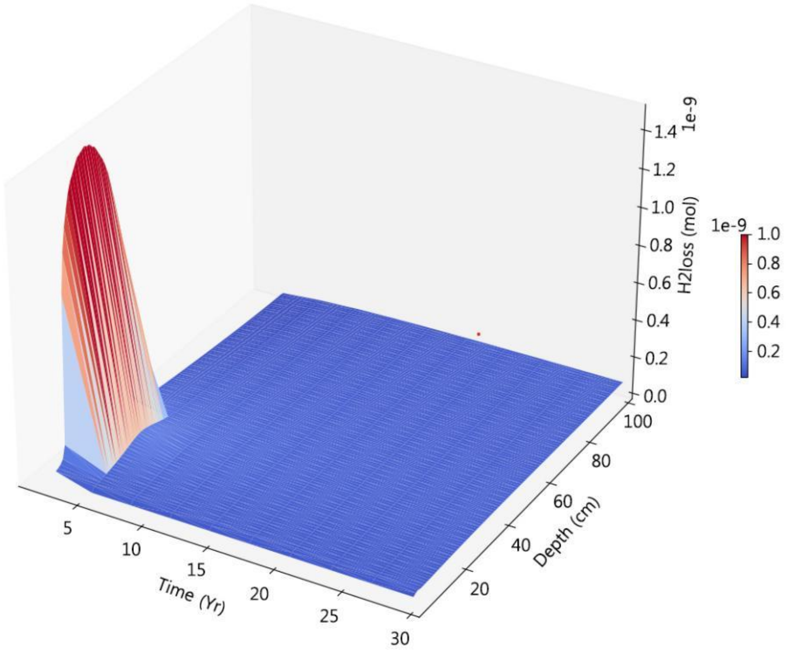


Figure 5. 3. Case3-$H_2$ loss when T=80℃ P=100atm

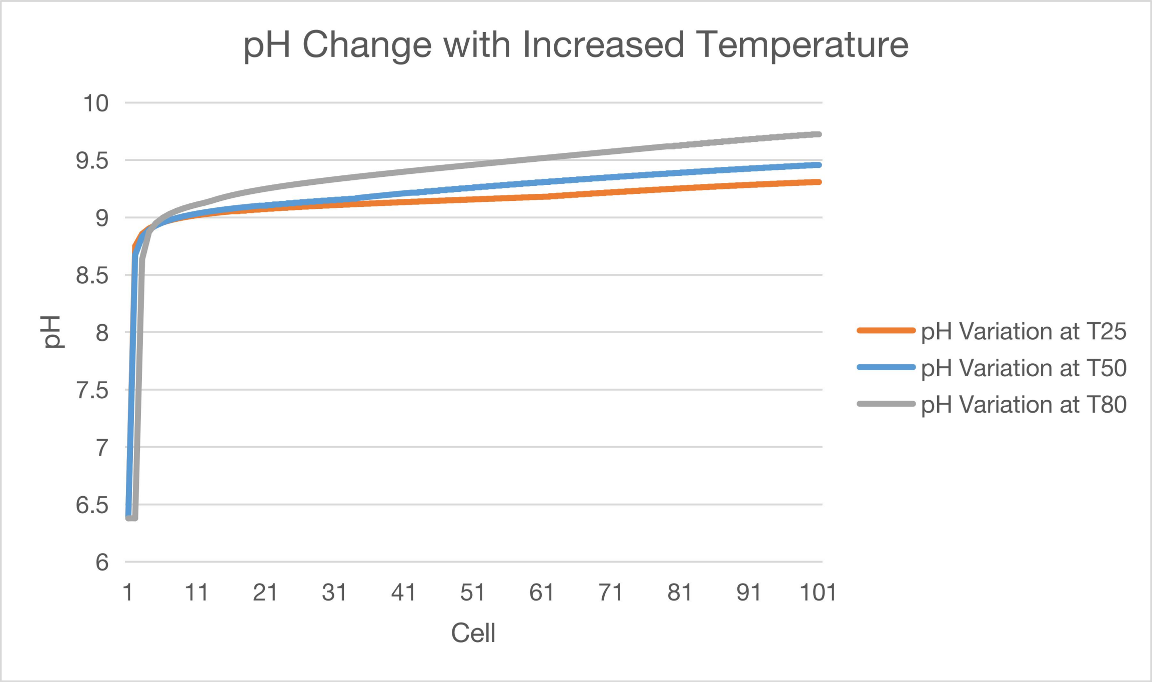


Figure 5. 4. pH variation at 3rd year

### 5.3.2 Pressure variation with fixed low temperature (25℃)

It is confidently to observe that pressure variation has limited impacts on diffusion process at low temperature zone. For instance, as pressure increasing, hydrogen diffusion loss before equilibrium has almost constant increment, and this increment is located mainly at first 25cm depth within first 5 years.

This constant hydrogen diffusion loss is caused by the mechanism of hydrogen partial pressure gradient between two ends, and thus slightly elevating the diffusion rate. Different from temperature increment cases, there is no significant hydrogen loss variation when increasing pressure from 100atm to 300atm, the diffusion time taking to equilibrium is also not strikingly shorter, and even no further significant hydrogen loss variation after equilibrium point. It is inconsistent with previous researcher proposed hypothesis "hydrogen partial pressure increment is likely causing higher diffusion loss[53]" Their fundamental is based on the Law of Eras Diffusion[18, 33], gas diffusion rate is directly proportional to gaseous partial pressure gradient and inversely proportional to the square root of gaseous density or molecular weight. Which indicates that hydrogen as lightest molecules and is supposed to express higher diffusion rate. Nevertheless, by considering hydrogen diffusion loss in aqueous phase, diffusion rate is mainly dependent on gas dissolution rate in specific aqueous solution, the hydrogen solubility in brine is extremely low and is not significantly increasing with only pressure elevating [54, 142, 143]. Especially in low temperature cases, there is lack of kinetic energy to support more dissolved hydrogen molecules diffusing from high pressure end to low pressure end [108, 143, 154, 155]. Overall, the diffusive aqueous hydrogen loss of three different pressure cases is constantly in $3 \times 10^{-10}$moles, this also matches with pH profile in Figure 5.7, which gives similar pH trend in three cases and representing similar hydrogen loss across 100cm caprock depth. Thus, it is confirmed that pressure elevation has negligible impacts on hydrogen diffusion loss under low temperature condition. To be more accurately ensure that pressure elevation impacts on diffusion hydrogen loss, it is further studied diffusion profile with high fixed temperature (70℃).

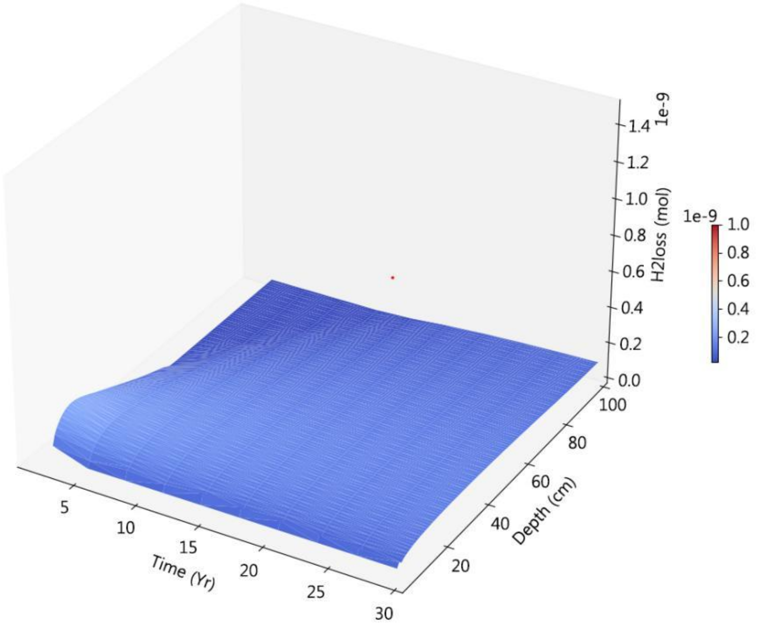


Figure 5. 5. Reference Case1-when T=25℃ and P=100atm

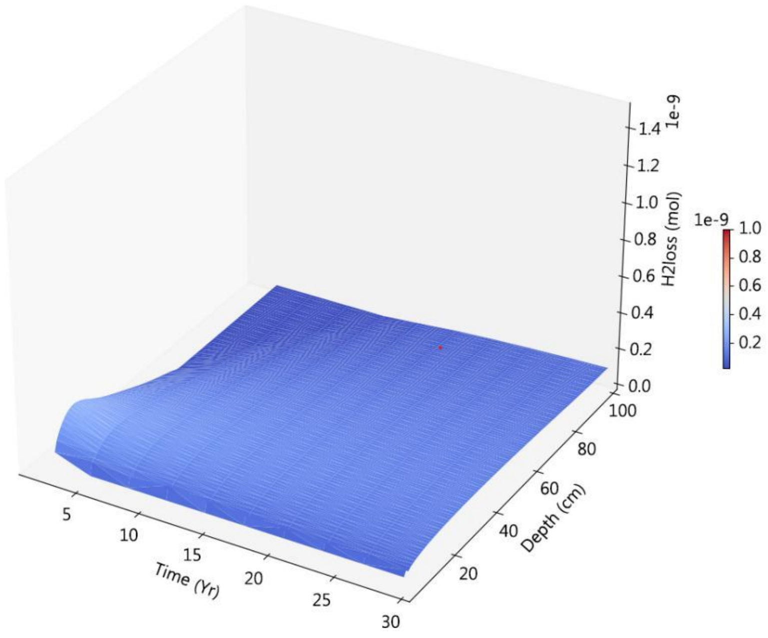


Figure 5. 6. Case4-when T=25℃ and P=200atm

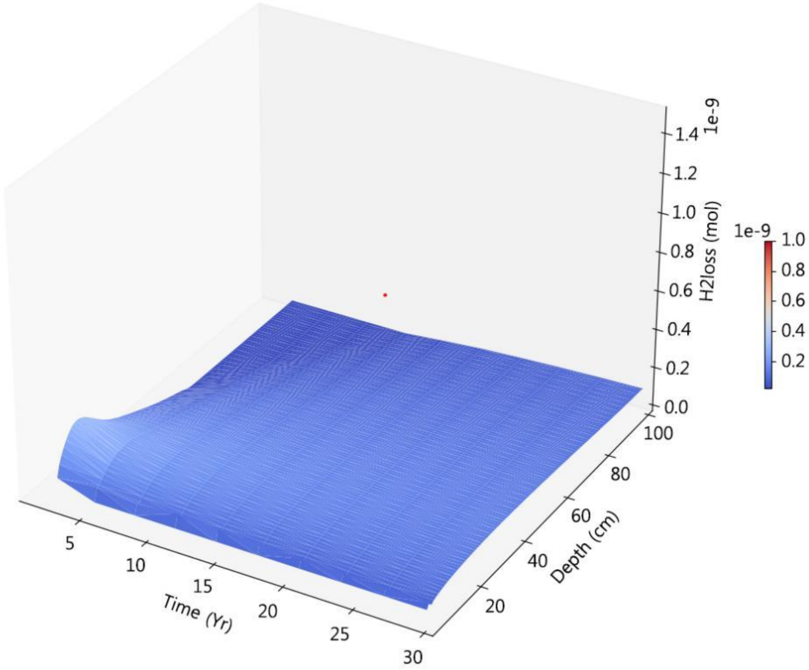


Figure 5. 7. Case5-when T=25℃ and P=300atm

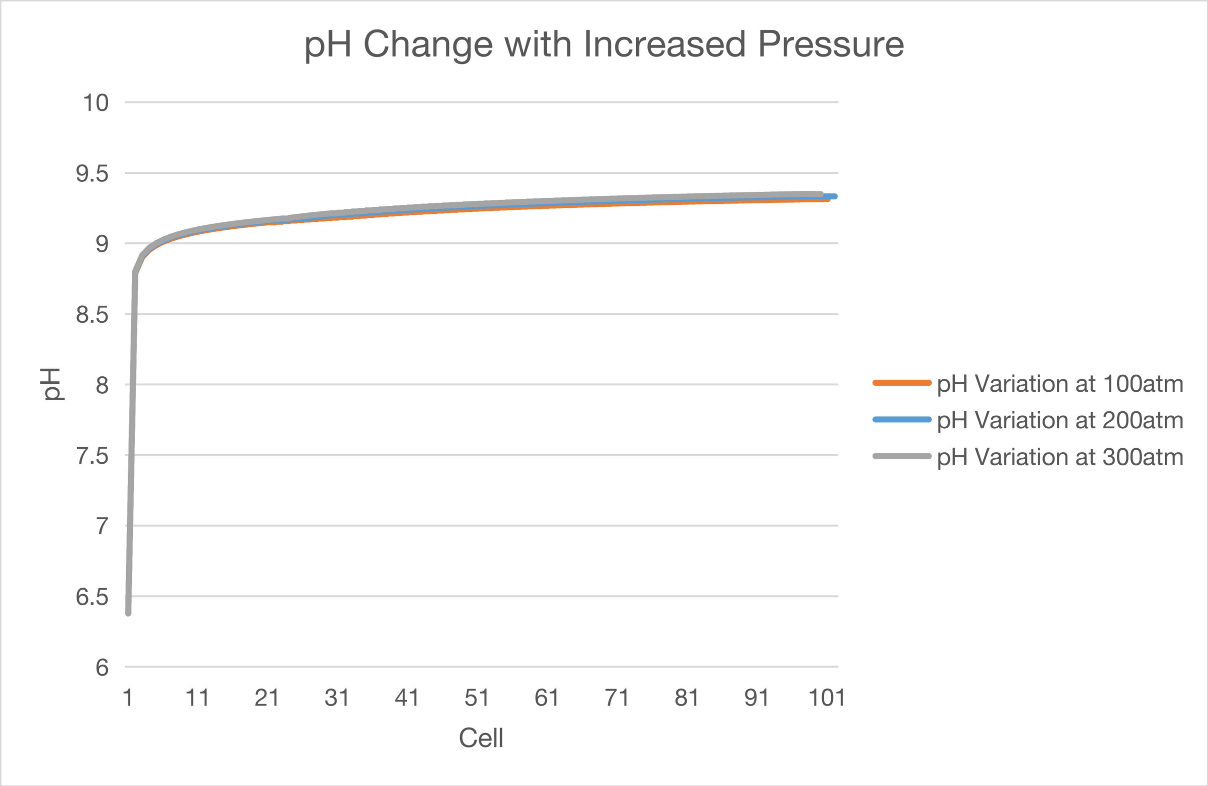


Figure 5. 8. pH variation at 3rd year

### 5.3.3 Pressure variation with fixed high temperature (70℃)

Based on the experiments conducted at a fixed high temperature (70℃), it is observed that pressure variations have a significant impact on the instant loss of hydrogen in the high temperature zone. The peak loss is much higher in the fixed high temperature (70℃) scenarios compared to the negligible impact on instant hydrogen loss observed in the fixed low-temperature (25℃) cases, where hydrogen loss increases from $0.8\times10^{-9}$ moles to $1.3\times10^{-9}$ moles with pressure elevation from 100 atm to 300 atm. This is because increasing the fixed temperature increment within 30 years of storage time causes a higher hydrogen molecular concentration in the aqueous phase, which provides kinetic energy to trigger hydrogen molecules movement under pressure variation conditions[156, 157]. However, under the ambient pressure temperature condition, there is insufficient molecular activity to initiate hydrogen concentration difference, and thus pressure elevation provides invisible hydrogen loss variation due to a lack of initial molecules' kinetic energy[158, 159].

Another important observation from the high-temperature (70℃) cases is that equilibrium time increases with increasing pressure. For instance, in listed figures 5.9 to 5.11, an increase in pressure of every 100 atm results in the requirement of an additional 5 years to reach equilibrium. This is because the diffusion rate slows down as the molecules pack denser. Although different molecules migrate with a certain mean velocity depending on the temperature in physics, the substances move at a much lower velocity than the mean velocity of molecular free motion[160, 161]. When pressure is elevated, the molecules pack denser, which means there is less free-path length, further slowing down the diffusion rate and resulting in a longer time to reach equilibrium state. [162-165]. This finding is in consistent with Jingyu Liu's report[166] that pressure increment causes higher fluid density and lower hydrogen diffusivity, which restrains hydrogen diffusion rate. However, this slowed diffusion rate resulting from pressure elevation has no significant impact on diffusion length depth, which can be observed as an average of 50 cm in all high-temperature and pressure cases. This is due to the limited hydrogen dissolution capacity in brine, which is insufficient to provide a strong mechanism from concentration difference[140, 167, 168]. Therefore, pressure mainly impacts longer diffusion time, and no potential aqueous hydrogen loss was observed within the 300 atm pressure range.

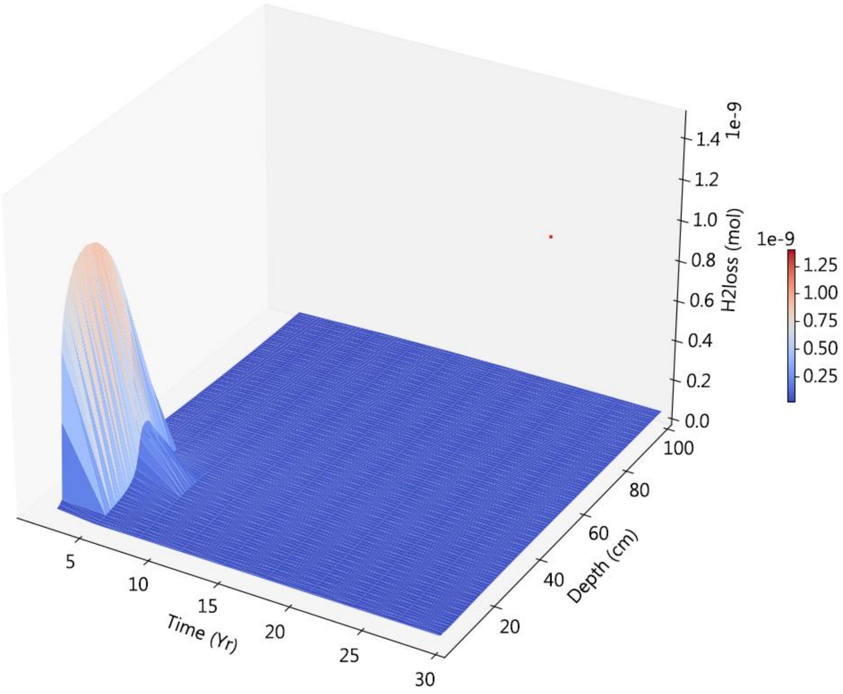


Figure 5. 9. Case6 – when T=70℃ and P=100atm

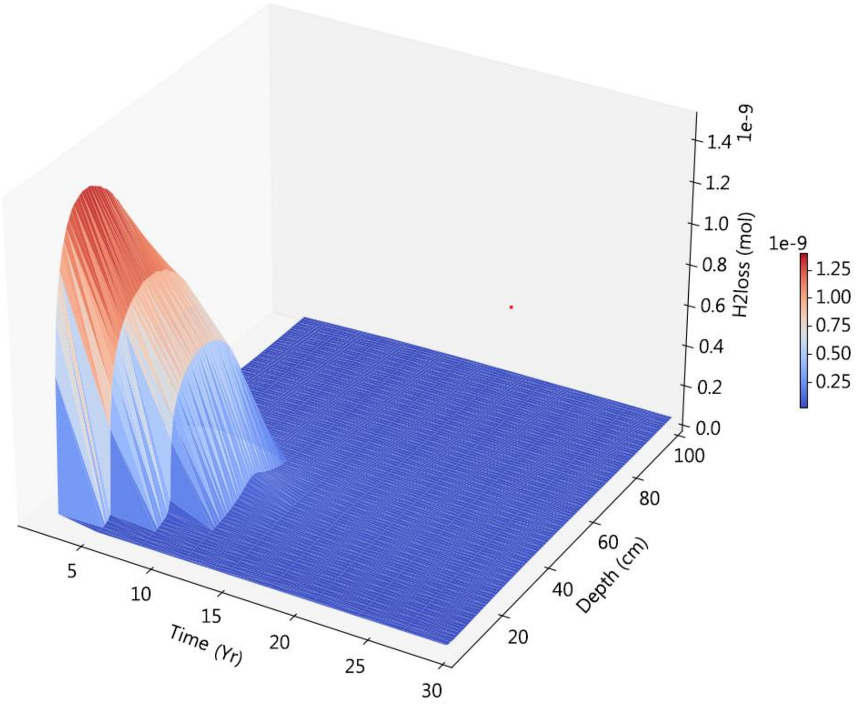


Figure 5. 10. Case7 – when T=70℃ and P=200atm

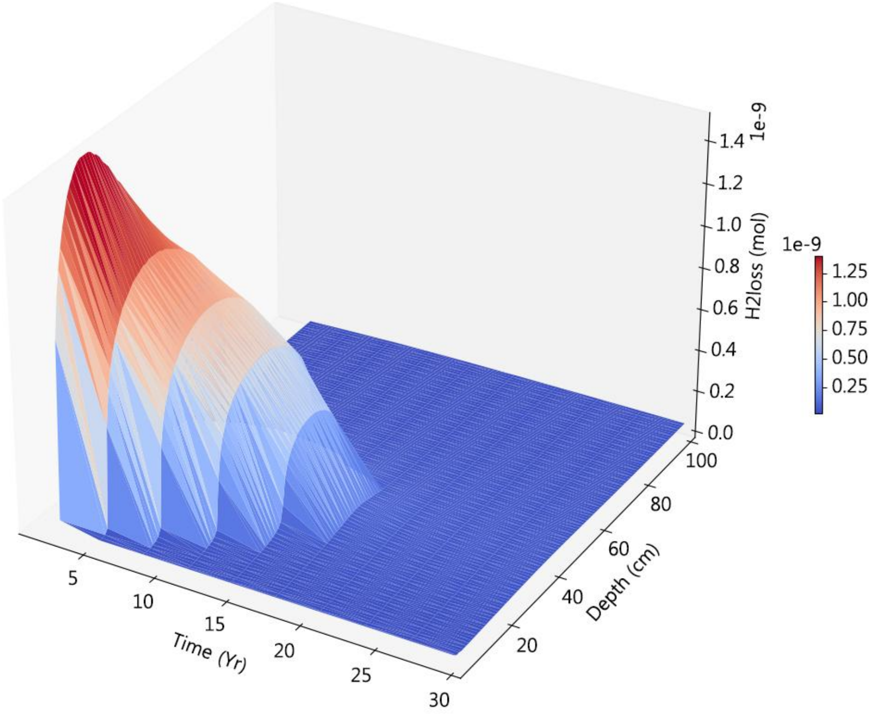


Figure 5. 11. Case8 – when T=70℃ and P=300atm

## 5.4 Conclusions

The hydrogen porous medium storage is considered to be a promising solution for advancing hydrogen energy development. Therefore, it is crucial to investigate the potential risk of hydrogen loss in the diffusion process. This study aimed to establish 8 kinetic simulation cases to evaluate the effects of pressure and temperature elevation on diffusion depth, equilibrium time, and hydrogen loss over a period of 30 years storage time. The results showed that hydrogen diffusion depth was not more than 60cm out of a total of 100cm in all tested temperature and pressure cases. The diffusion depth was mainly dependent on the concentration of hydrogen molecules in brine. Moreover, a significant increase in temperature enhances hydrogen solubility in brine, leading to a higher instantaneous hydrogen loss rate. However, pressure elevation only reduces the diffusion rate and increase the time required to reach system equilibrium. In conclusion, our results showed that no significant aqueous hydrogen penetration was observed in diffusion activity within the temperature range of 25℃ to 80℃ and pressure range of 100atm to -300 atm in poor-carbonates reservoirs. This kinetic diffusion simulation analysis provides a reliable reference for future underground hydrogen storage risk assessments, indicating that there is no apparent risk of aqueous diffusion hydrogen loss in the tested conditions.

# Chapter 6. Concluding Remarks and Future Works Outlook

Hitherto, large-scale underground hydrogen storage has been widely discussed and studied. This type of storage is potential to stimulate hydrogen energy development by providing safe and economical solution in its storage assessment plan [36, 169]. However, not all subsurface formation is suitable for hydrogen storage since hydrogen as a smallest molecule with active chemical nature can react with various minerals, which likely triggers mineral dissolution and precipitation, resulting in hydrogen consumption and contamination [82]. In addition, there may be dissolved oxygen presenting at subsurface and possibly acting as oxidizing agents to trigger redox reaction among hydrogen, brine, and certain groups of minerals[53, 139]. Therefore, qualitative understanding of impact of hydrogen-brine-mineral interactions on mineral dissolution and precipitation and its implications on caprock and hydrogen storing condition remain challenging due to the lack of fundamental studies on the geochemical driven at subsurface.

Caprock seal capacity is also of vital importance to underpin the success of hydrogen underground storage in terms of preventing from stored hydrogen leakage. When caprock mineral dissolution is triggered, the caprock integrity, mineralogy, porosity and permeability may be negatively affected and thus resulting in hydrogen storage sealing risks [170, 171]. In addition, hydrogen dispersion loss through caprock is becoming a rising concern in hydrogen underground risk matrix. This is due to the fact that hydrogen as the smallest molecule has a higher dispersion coefficient compared to methane, which likely leads to a certain hydrogen loss through the caprock even without pre-existing factures [18, 172]. Therefore, it is essential to predict hydrogen dispersion profile and estimate minimum caprock thickness to prevent hydrogen storage from unwanted loss.

This study aims to quantitatively investigate the role of hydrogen-brine-rock interactions through geochemical modelling and understand its impact on caprock integrity during hydrogen underground storage. Several simulation models were established to analyse (1) impacts of redox reaction on mineral dissolution and precipitation, pH variation, hydrogen solubility change, hydrogen conversion and contamination, and (2) role of diffusion activity in underground storage in terms of caprock integrity and hydrogen loss. Geochemical modelling tool (PHREEQC Version 3) and one data interpretation tool (Spyder with Python language) have been applied to draw a geochemical interaction profile through batch modelling. The main conclusions are obtained as follows.

## 6.1 Role of Redox Reactions during Hydrogen Underground Storage in Porous Media

- Mineral dissolution in quartz and pyrite systems have negligible impact on caprock integrity (less than 0.05% mineral dissolution) and hydrogen loss (less than 1.0) across all simulation temperature (20 $^{\circ}C - 200^{\circ}C$) and pressure (1atm - 1000atm), which unlikely affects caprock integrity.
- Hydrogen solubility plots and pH plots of quartz and pyrite system show similar tendency as non-mineral system, which indicates that hydrogen dissolution and dissociation in these two systems are mainly contributed by temperature elevation, causing higher gas solubility regardless of mineral effect.
- The minor mineral dissolution also eliminates the risk from hydrogen loss since hydrogen-brine-rock geochemical interactions hardly take place without dissolved minerals.
- Carbonates minerals are considered as sensitive minerals in underground hydrogen storage site. This is because calcite and siderite show significant mineral dissolution (almost fully dissolved) and hydrogen loss (up to 41%) based on the static batch modelling. However, it is worth noting that the geochemical database used in this study may have already incorporated the impact of the microbial on the equilibrium constant and enthalpy. We believe that more quantitative experimental work needs to be conducted to characterize the abiotic and biotic geochemical reactions in the future.
- The methane production decreases with increasing temperature in a calcite system, whereas $CH_4$ production keeps constant across all temperature and pressure in siderite system. The enthalpy of siderite dissolution indicates better resistance on temperature change. Therefore,

the siderite system shows no decremented tendency in either mineral dissolution plots or methane generation plots.

## 6.2 Impact of Hydrogen Dispersion through Caprock on Hydrogen loss and Its Implications for Underground Hydrogen Storage

- Hydrogen dispersion takes place up to 1 meter through caprock, which shows a minor role in caprock sealing and integrity.
- The hydrogen loss increases with increasing temperature under fixed pressure at 100 atm. This is because temperature elevation provides molecules kinetic energy, which forces more hydrogen dissolution in brine and further leading to hydrogen ions concentration difference, and hydrogen diffusion activity will be temporarily intensified until two reach equilibrium state.
- The time in reaching dispersion equilibrium is shorter in high temperature cases. This is because a higher temperature provides more molecules kinetic energy and it will not only enhance hydrogen ions concentration difference, also intensify a higher diffusion rate, resulting in less time to reach dispersion equilibrium.
- Pressure variation plays a negligible role in hydrogen loss. Increasing pressure requires more time to reach in dispersion equilibrium, especially in high fixed temperature case. This is because when pressure increases, the molecules is packing denser, which means less free-path length, and further slowing down the diffusion rate [162-165], hence requires longer time to reach in equilibrium.

## 6.3 Future Works Outlook

In this work, we have studied the impacts and implications of hydrogen-fluid-rock geochemical interactions on caprock integrity, which may shed lights on large-scale hydrogen underground storage in porous media. However, more quantitative work remains to be carried out to understand the impact of the geochemical reactions on geo-mechanical behaviour of caprocks, which is suggested as follows.

- From geochemical perspective, current studies show that carbonates minerals may lead to aqueous hydrogen loss and mineral dissolution in particular with corresponding microbials. There is an urgent need to investigagte whether carbonates biotic geochemical dissolution leads to caprock and wellbore geo-mechanical properties variation in terms of Young’s modulus, stress and strain.
- For reservoirs with a certain amount of calcite as cement, it is important to understand the distribution and allocation of the calcite cement at pore scale. For example, the impact of hydrogen on reservoir integrity may be minor for calcite-filled pores, compared to calcite as a

cement distributed at contact areas of grains. However, this needs to be tested and examined with further experimental work in particular with biotic geochemical reactions.

- Furthermore, another common feature at subsurface formation is faults and fractures. To date, there is lack of studies based on hydrogen conditioned geo-mechanical analysis in faults and fractures region. Therefore, core samples with existing fractures need to be tested with hydrogen aging process to quantity the risks of fault slip due to the reactions between hydrogen and fracture filled minerals.

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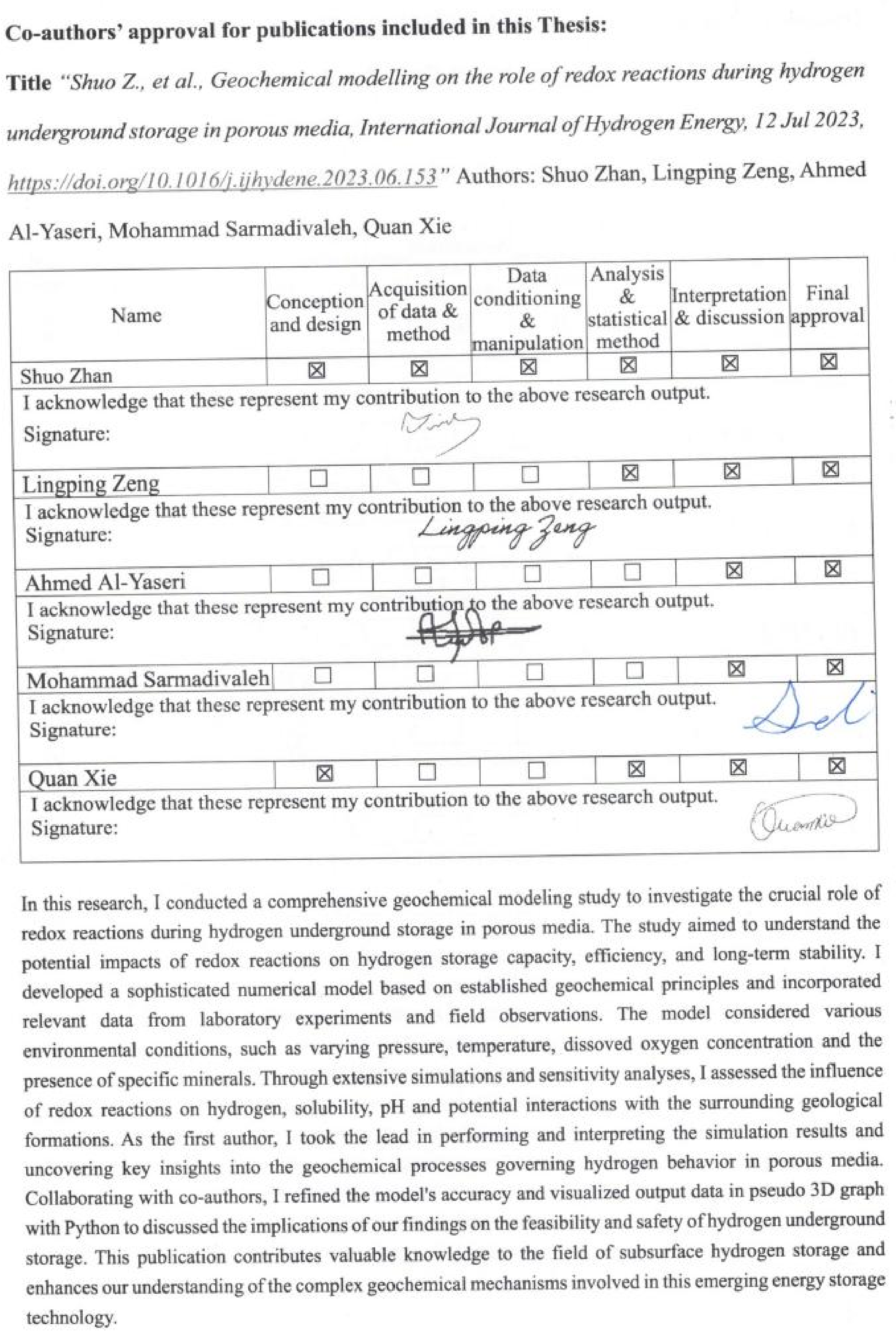
# Attribution Statement



**Co-authors' approval for publications included in this Thesis:**

**Title** *"Shuo Z., et al., Geochemical modelling on the role of redox reactions during hydrogen underground storage in porous media, International Journal of Hydrogen Energy, 12 Jul 2023, https://doi.org/10.1016/j.ijhydene.2023.06.153"* Authors: Shuo Zhan, Lingping Zeng, Ahmed Al-Yaseri, Mohammad Sarmadivaleh, Quan Xie

| Name | Conception and design | Acquisition of data & method | Data conditioning & manipulation | Analysis & statistical method | Interpretation & discussion | Final approval |
|---|---|---|---|---|---|---|
| Shuo Zhan | ☒ | ☒ | ☒ | ☒ | ☒ | ☒ |
| I acknowledge that these represent my contribution to the above research output.<br>Signature: | | | | | | |
| Lingping Zeng | ☐ | ☐ | ☐ | ☒ | ☒ | ☒ |
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| Ahmed Al-Yaseri | ☐ | ☐ | ☐ | ☐ | ☒ | ☒ |
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| Mohammad Sarmadivaleh | ☐ | ☐ | ☐ | ☐ | ☒ | ☒ |
| I acknowledge that these represent my contribution to the above research output.<br>Signature: | | | | | | |
| Quan Xie | ☒ | ☐ | ☐ | ☒ | ☒ | ☒ |
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In this research, I conducted a comprehensive geochemical modeling study to investigate the crucial role of redox reactions during hydrogen underground storage in porous media. The study aimed to understand the potential impacts of redox reactions on hydrogen storage capacity, efficiency, and long-term stability. I developed a sophisticated numerical model based on established geochemical principles and incorporated relevant data from laboratory experiments and field observations. The model considered various environmental conditions, such as varying pressure, temperature, dissoved oxygen concentration and the presence of specific minerals. Through extensive simulations and sensitivity analyses, I assessed the influence of redox reactions on hydrogen, solubility, pH and potential interactions with the surrounding geological formations. As the first author, I took the lead in performing and interpreting the simulation results and uncovering key insights into the geochemical processes governing hydrogen behavior in porous media. Collaborating with co-authors, I refined the model's accuracy and visualized output data in pseudo 3D graph with Python to discussed the implications of our findings on the feasibility and safety of hydrogen underground storage. This publication contributes valuable knowledge to the field of subsurface hydrogen storage and enhances our understanding of the complex geochemical mechanisms involved in this emerging energy storage technology.

**Co-authors' approval for manuscript included in this Thesis:**

**Title** *"Impact of Hydrogen Diffusion through Caprock on Hydrogen Loss in Underground Hydrogen Storage"* Authors: Shuo Zhan, Lingping Zeng, Ahmed Al-Yaseri, Yongqiang Chen, Mohammad Sarmadivaleh, Quan Xie **(Under Review)**

| Name | Conception and design | Acquisition of data & method | Data conditioning & manipulation | Analysis & statistical method | Interpretation & discussion | Final approval |
|---|---|---|---|---|---|---|
| Shuo Zhan | ☒ | ☒ | ☒ | ☒ | ☒ | ☒ |
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| Lingping Zeng | ☐ | ☐ | ☐ | ☒ | ☒ | ☒ |
| I acknowledge that these represent my contribution to the above research output.<br>Signature: Lingping Zeng | | | | | | |
| Ahmed Al-Yaseri | ☐ | ☐ | ☐ | ☐ | ☒ | ☒ |
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| Yongqiang Chen | ☐ | ☐ | ☐ | ☐ | ☒ | ☒ |
| I acknowledge that these represent my contribution to the above research output.<br>Signature: Yong qiang CHEN | | | | | | |
| Mohammad Sarmadivaleh | ☐ | ☐ | ☐ | ☐ | ☒ | ☒ |
| I acknowledge that these represent my contribution to the above research output.<br>Signature: | | | | | | |
| Quan Xie | ☒ | ☐ | ☐ | ☒ | ☒ | ☒ |
| I acknowledge that these represent my contribution to the above research output.<br>Signature: Quanxie | | | | | | |

In this study, I conducted comprehensive research to investigate the impact of hydrogen diffusion through caprock on hydrogen loss in underground hydrogen storage. The project involved geochemical model designing and executing a comprehensive series of simulation to quantify hydrogen diffusion loss and penetration depth in multi-minerals caprock materials. This simulation involved the use of advanced PHREEQC software to model hydrogen loss from molecular diffusion through caprock pores. Therefore, I developed a numerical model to simulate the diffusion process and assess the implications for 30 years of storage time. As the first author, I was responsible for performing and interpreting the numerical data, identifying key trends, and drawing meaningful conclusions. I actively collaborated with co-authors to refine the analysis and ensure the scientific rigor of the study. The findings of this research shed light on the factors influencing hydrogen loss in underground storage and provide valuable insights for optimizing storage design and operational strategies in the context of emerging hydrogen-based energy systems."