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Assessment of biochemical and chemical effects

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Feasibility of hydrogen storage in depleted hydrocarbon chalk reservoirs: Assessment of biochemical and chemical effects

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HIGHLIGHTS

- Abiotic reactions alone cannot be a risk for hydrogen storage in chalk reservoirs.
- Biotic reactions may cause a maximum hydrogen loss of below 0.6% per year.
- Many North Sea chalk reservoirs are riskless for underground hydrogen storage.
- Souring can impose temporal economic and environmental risks to hydrogen storage.

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ABSTRACT

Hydrogen storage is one of the energy storage methods that can help realization of an emission free future by saving surplus renewable energy for energy deficit periods. Utilization of depleted hydrocarbon reservoirs for large-scale hydrogen storage may be associated with the risk of chemical/biochemical reactions. In the specific case of chalk reservoirs, the principal reactions are abiotic calcite dissolution, acetogenesis, methanogenesis and biological souring. Here, we use PHREEQC to evaluate the dynamics and the extent of hydrogen loss by each of these reactions in hydrogen storage scenarios for various Danish North Sea chalk hydrocarbon reservoirs. We find that: (i) Abiotic calcite dissolution does not occur in the temperature range of 40–180°C. (ii) If methanogens and acetogens grow as slow as the slowest growing methanogens and acetogens reported in the literature, methanogenesis and acetogenesis cannot cause a hydrogen loss more than 0.6% per year. However, (iii) if they proceed as fast as the fastest growing methanogens and acetogens reported in the literature, a complete loss of all injected hydrogen in less than five years is possible. (iv) Co-injection of CO2 can be employed to inhibit calcite dissolution and keep the produced methane due to methanogenesis carbon neutral. (v) Biological sulfate reduction does not cause significant hydrogen loss during 10 years, but it can lead to high hydrogen sulfide concentrations (1015 ppm). Biological sulfate reduction is expected to impact hydrogen storage only in early stages if the only source of sulfur substrates are the dissolved species in the brine and not rock minerals. Considering these findings, we suggest that depleted chalk reservoirs may not possess chemical/biochemical risks and be good candidates for large-scale underground hydrogen storage.

1. Introduction

Hydrogen is currently the center of attention as a major clean energy carrier to decarbonize energy demanding sectors such as transport and heating [1–5]. The United Nations Industrial Development Organization has described hydrogen as a true paradigm shift for energy storage on commercial scales, particularly for renewable energy sources [6]. In the IPCC’s 1.5 °C report hydrogen is claimed to play a vital role to restrict global warming and reduce CO2 emissions from energy intensive industries [7].

Renewable energy resources such as wind and solar energy - unlike geothermal energy [e.g. 8,9] - are intermittent, as they depend on seasonally fluctuating atmospheric events such as sunlight intensity/duration and wind force [10,11]. Since the annual variations of the energy demand do not follow the same trend as renewable energy production, renewable energy supply is challenged by excess and deficit...
periods, and energy storage is required to meet the whole system demand [12,13]. For example, surplus renewable energy can be converted to hydrogen by utilizing electrolysis (green hydrogen) [14] and then the produced hydrogen can be stored for usage during high energy demand periods [15]. Hydrogen can also be produced by reformation of fossil fuels (grey hydrogen) which can result in reducing emissions if it is combined with carbon capture and storage (blue hydrogen) [15].

Surface facilities such as pipes or tanks can only store hydrogen in the MWh order of magnitude, providing energy for only for hours to days. Subsurface storage is inevitable for energy storage in the range of GWh to TWh. Among various subsurface settings, salt caverns have been used commercially over the past few decades in the United States, Britain and Germany [16,17]. Salt caverns are extremely gas-tight (with a theoretical leakage rate of 0.01% per year) and relatively inert to hydrogen [18]. Salt caverns are ideal for short- to medium-term storage since they allow high injection/withdrawal rates, enabling multiple storage-production cycles per year [18,19]. Hydrogen storage in salt caverns is constrained by pressures below 20 MPa [20] and the presence of salt formations with an appropriate thickness, limiting their storage capacity to hundreds of GWh [21]. Saline aquifers and depleted hydrocarbon reservoirs are geographically more available and have storage capacities several orders of magnitude higher than those of the salt caverns [22,23]. Compared to depleted hydrocarbon reservoirs saline aquifers require exploration and discovery that is costly [24]. Moreover, saline aquifers are filled with water with a pressure that can be assumed to be the hydrostatic pressure. Thus, hydrogen storage requires displacement of the currently filling brine creating pressures above hydrostatic pressure [25]. Depleted oil and gas reservoirs benefit from an already well-known geological setting with proven gas tightness for over millions of years, and pore spaces at pressures below hydrostatic pressure due to hydrocarbon production. Their applications include the co-injection of hydrogen and CO₂ to promote the production of carbon neutral methane by methanogenesis (the Hychico project in Argentina, [26] and the Underground Sun Conversion in Austria [27]) but they have not been used for hydrogen storage alone.

Underground hydrogen storage risks are either geomechanics dependent or reaction (microbial/geochemical) dependent. As geomechanics dependent risks for both salt caverns and porous rocks have been studied elsewhere [28,29], here we solely focus on reaction dependent risks since they are among the key factors preventing the implementation of hydrogen storage in depleted hydrocarbon reservoirs [30]. Both microbial and chemical reactions threaten hydrogen storage in depleted hydrocarbon reservoirs by hydrogen consumption and the consequent hydrogen loss as well as alteration of reservoir properties [30]. Souring via hydrogen sulfide (H₂S) formation, microbial-induced plugging via mineral precipitation and biofilm formation, and dissolution of minerals are some examples of unwanted microbial reactions [31]. Chemical reactions of hydrogen with the reservoir rock include but are not limited to modification of the rock mineral assemblage by creating new minerals or mineral dissolution/precipitation [32,33]. A change in rock mineralogy could lead to a change in several reservoir properties, especially the porosity and permeability. This may adversely affect the storage capacity of a reservoir, and the injectivity and withdrawal of the stored hydrogen.

The induced reactions due to hydrogen storage have been investigated through various experimental and modeling/theoretical methodologies. For abiotic reactions, experimental studies have been done on cores [34] or crushed rock/mineral powder mixes placed in reactors with given temperature and pressures [33]. Biotic reactions have been studied through growth experiments at different temperatures, salinities, pressures and temperatures (detailed review can be found in [35]). Calculation of free energy of reaction has been employed to investigate mono mineral reactions/interactions of hydrogen with various minerals typically found in underground reservoirs [36]. Various modeling software such as CMG, Eclipse, COMSOL, DuMuX, OpenGeoSys, OPM, GWB, and TOUGHREACT have been used to investigate the feasibility of UHS considering hydrogeochemical, geophysical and biological mechanisms. However, for studying hydrogeochemical effects, PHREEQC [37] has been the most widely-used tool [38–40].

There is limited knowledge about the potential hydrogen loss due to microbial reactions in a hydrogen storage setting. Various works highlighted how variations in physiochemical conditions such as temperature, salinity and pH control the activity of hydrogen consuming microorganisms directly (e.g. [35,41]). Yet, the indirect influence of temperature on hydrogen consuming metabolisms via the temperature effect on the solubility of various minerals that can either act as a buffer, or as a source for providing terminal electron acceptors, is unknown. Furthermore, to the best of our knowledge, it is not known whether hydrogen storage can biotically trigger calcite dissolution. Addressing these knowledge gaps could reveal whether chalk reservoirs as one of the major types of underground reservoirs can be used for hydrogen storage. We used PHREEQC [37] to quantify hydrogen consumption via the biotic reaction of hydrogen with calcite as well as the major biotic H₂-consuming reactions (acetogenesis, souring and methanogenesis). Four different types of formation brine [42], corresponding to fourteen hydrocarbon reservoirs in the Danish North Sea, were considered [43]. To assess a worst case scenario for the loss of hydrogen due to microbial activity, our model used the fastest growth rates for each microbial metabolism that have been reported in the literature. Additionally, we assessed the possibility of simultaneous hydrogen storage-CO₂ capture as a solution to keep the energy bioconversion from hydrogen to methane carbon neutral. Finally, using a case study, we showed how the developed knowledge in this work can be used to screen a chalk reservoir for its suitability for hydrogen storage.

2. Material and methods

2.1. Conceptual model

Fig. 1 demonstrates the conceptual 0D-model utilized in this work which takes into account three phases of gas, water and rock. For the sake of simplicity, for all the simulations we assumed a unit volume of the reservoir consisting of 1 L of water, 7.679 L of calcite and 1.15 L of hydrogen gas at initial pressure of 351 bar. This corresponds to a porosity of 21.9% and water saturation (Sw) of 47%.

Four different water compositions as listed in Table 1 were considered to study the possibility of calcite dissolution during hydrogen storage. Each formation type represents the brine composition of some hydrocarbon reservoirs (Table 1) [42]. Different species depending on their saturation index can precipitate, dissolve or partition to the gas phase. Interactions between gas, water and solid phases (dissolution, precipitation and partitioning) are considered to be equilibrium reactions while microbial reactions are considered to be kinetic reactions. PHREEQC version 3 provided by US geological survey [37] was used for the modeling. PHREEQC calculates the concentration of different species in different phases by equilibrium calculation, e.g. at each time step the concentration of hydrogen in water phase is calculated based on hydrogen partial pressure and concentration of various ions such as bicarbonate are calculated considering dissolution/precipitation of various carbonate minerals such as calcite and dolomite. LLNL thermodynamic database was used to calculate chemical speciation and activity of species [44]. The database is valid for the temperature range of 0 to 300 °C. The impact of pressure on activity coefficients is ignored under the pressures of interest in this study [46].

It was assumed that no microbial metabolism produced any byproducts that could inhibit another metabolism. Besides the electron
donor and acceptor, each metabolic pathway needs a nitrogen source such as ammonium and a carbon source such as acetate. We assumed that the only limiting nutrients for a metabolism are its electron donor or acceptors, and negligible sulfate mineral dissolution limiting the available sulfate to the initial brine contents. While the initial gas phase is hydrogen at 351 bar, various chemical reactions may change the gas phase composition and pressure.

2.2. Reaction model

Microbial reactions are composed of two individual reactions called anabolism and catabolism. The metabolic reaction is the sum of the catabolic reaction and the anabolic reaction multiplied by anabolism and catabolism. The metabolic reaction is the sum of the

Table 1
The North Sea DUC reservoirs and their formation brine type and composition [42].

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Type 1</th>
<th>Type 2</th>
<th>Type 3</th>
<th>Type 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Roar, Tyra SE, Valdemar</td>
<td>Harald east, S. Arne</td>
<td>Dagmar, Gorm, Kraka, Regnar, Rolf</td>
<td>Dan, Halldan, Skjold</td>
</tr>
</tbody>
</table>

| Na (mg/L) | 11,400 | 31,400 | 22,800 | 18,300 |
| k (mg/L)  | 179    | 578    | 372    | 395    |
| Cl (mg/L) | 18,500 | 58,100 | 50,200 | 32,400 |
| Ca (mg/L) | 497    | 5590   | 2030   | 989    |
| Mg (mg/L) | 175    | 889    | 328    | 573    |
| Sr (mg/L) | 1060   | 11,000 | 5460   | 1900   |
| Ba (mg/L) | 22.3   | 330    | 2.24   | 6.92   |
| SO4 (mg/L)| 21.3   | 18.4   | 592    | 1250   |
| TDS (M NaCl) | 0.547 | 1.85   | 1.40   | 0.954  |

Fig. 1. The schematic of the geochemical model used to study hydrogen storage feasibility in depleted carbonate hydrocarbon reservoirs. Note that the liquid phase is in equilibrium with calcite and pure hydrogen gas is at a pressure of 351 bar.

for the metabolism in the work of Smeaton et al. (2018) [47], reactions a-c can be written to represent souring, methanogenesis and acetogenesis, respectively:

\[
\begin{align*}
\text{(a)} & \quad 0.028 \text{C}_2\text{H}_4\text{O}_2 + 0.024 \text{HCO}_3^- + 0.016 \text{NH}_4^+ + \text{H}_2\text{SO}_4^\text{aq} + 0.236 \text{SO}_4^{2-} + 0.272\text{H}^+ \rightarrow 0.08 \text{CH}_4\text{O}_2\text{N}_2\text{O}_2^+ + 0.236 \text{H}^+ + 1.03 \text{H}_2\text{O} \\
\text{(b)} & \quad 0.264 \text{HCO}_3^- + \text{H}_2\text{SO}_4^\text{aq} + 0.006 \text{NH}_4^+ + 0.258\text{H}^+ \rightarrow 0.03 \text{CH}_4\text{O}_2\text{N}_2\text{O}_2^+ + 0.234 \text{CH}_4\text{O}_4^\text{aq} + 0.778 \text{H}_2\text{O} \\
\text{(c)} & \quad 0.499 \text{HCO}_3^- + \text{H}_2\text{SO}_4^\text{aq} + 0.004 \text{NH}_4^+ + 0.258\text{H}^+ \rightarrow 0.02 \text{CH}_4\text{O}_2\text{N}_2\text{O}_2^+ + 0.239 \text{C}_2\text{H}_2\text{O}_2^- + 1.01 \text{H}_2\text{O}
\end{align*}
\]

2.3. Kinetic model

For metabolism i with species A and D as the electron donor and acceptor, respectively, the metabolism rate can be described by Monod equation as follows:

\[ r_i = \frac{\mu_{\text{max}} C_i}{C_i + K_A + C_D + K_D} \]

(1)

where \( r_i [\text{MT}^{-1}] \) represents the rate of metabolism i, \( \mu_{\text{max}} [\text{T}^{-1}] \) is the specific growth rate, \( C_i [\text{M}] \) and \( K_m [\text{M}] \) are concentrations and half saturation constants for \( m = A, D \), respectively. The rate of consumption or production of component j (e.g. \( \text{NH}_4^+ \)) in metabolism i is then equal to \( r_j v_i \), where \( v_i \) is the stoichiometric coefficient of component j in metabolism i reaction. Table 2 lists a range of values for each of the parameters in equation (1) for each metabolic pathway.

As the availability of \( \text{CO}_2 \) has rarely been considered the limiting factor for methanogenesis or acetogenesis, there is little information about the corresponding \( K_A \) values. Dornseif et al. (1995) [49] reported 230 \( \mu \text{M} \) for the \( K_A \) of methanogenesis. Chen et al. (2019) [50]
showed that *Methanobacterium congolese* cannot metabolize HCO$_3^-$ in concentrations lower than 44.4 μM. In order to consider the worst case scenario, here we assume the lower limit for $K_A$ to be 1 μM and neglect the impact of variations in the $K_A$. Note that in this work the electron acceptors for methanogenesis and acetogenesis are considered to include all dissolved inorganic carbon (DIC) species, i.e. all the species with carbon at the oxidation state of +4 such as bicarbonate, CO$_3^{2-}$ (aq) and CaHCO$_3^-$.

Reactions a to c may change the pH of the solution as they have H$^+$ ion on their left hand side. In order to consider the dependency of the microbial metabolisms on the pH, the metabolism reaction rate $r_i$ can be multiplied with a coefficient $\gamma$ defined as [51]:

$$\gamma = \frac{(pH - pH_{min})(pH - pH_{max})}{(pH_{opt} - pH_{min})(pH_{opt} - pH_{max})}$$  \hspace{1cm} (2)

where $pH_{min}$ and $pH_{max}$ are the lowest and highest pH values, respectively, below or above which a given microbial process is inhibited, and $pH_{opt}$ is the pH value at which the microbial process occurs at maximal rate. As the reactions are expected to increase the pH, here we assume $pH_{min}$ and $pH_{opt}$ to be the same for all metabolisms and equal to a values of 4 and 7, respectively. For $pH_{max}$ we consider the values of 9 and 12.

Note that the kinetic model employed in this work does not consider the explicit impact of temperature on the growth rate of acetogens, methanogens and SRM in terms of its effect on the mean division rate. Additionally, our model assumes that macro nutrients such as N and P are not limiting.

### 2.4. Simulation design

In order to evaluate the solubility of calcite within temperature values observed for the studied hydrocarbon reservoirs, we first equilibrated the formation brine with calcite and then with hydrogen and determined calcite saturation index for temperature values in the range of 40–180 °C. Note that since the specific heat of hydrogen is significantly less than the specific heat of formation brine and reservoir rock, we assumed that hydrogen injection in the reservoir has an insignificant impact on the reservoir temperature. To investigate the consumption of hydrogen by microorganisms we assumed that the water phase is always in equilibrium with calcite and hydrogen. Four temperature values of 50, 75, 100 and 122 °C are considered here to represent the range of temperatures usually observed in hydrocarbon reservoirs. As biological sulfate reduction requires sulfate in the formation brine, we consider formation brine type 4 for souring with the highest sulfate content and type 1 with low sulfate content for methanogenesis and acetogenesis (Table 1). Each metabolism was evaluated separately assuming the other metabolisms were not active. Therefore here the cumulative effect of these metabolisms or their competition for hydrogen is not considered. In order to determine the best case scenario for hydrogen storage, we first considered the kinetic parameters corresponding to the slowest microbial growth rates (Table 2), i.e. lowest maximum specific growth rate $\mu$ and highest $K_s$ and $K_A$. We considered the opposite to investigate the worst case scenario. For souring only the worst case scenario was evaluated. As depleted chalk hydrocarbon reservoir contain an abundance of both organic and inorganic carbon sources [52], and because SRM are usually heterotrophs but have been observed to grow autotrophically and mixotrophically [53–55], we anticipated that only sulfate and hydrogen could limit souring. The maximum run time of simulations was considered to be 10 years, or the time required for complete hydrogen loss, or the time after which microbial reactions do not proceed any further.

### 2.5. Screening of various chalk hydrocarbon fields for hydrogen storage

Screening underground depleted reservoirs for their suitability to store gasses such as CO$_2$ and natural gas requires investigating various factors such as reservoir rock and fluid properties and type of reservoir trap [56]. However, here we solely screened reservoirs according to possible risks raised by chemical and biochemical reactions. As mentioned briefly in the introduction and in detail elsewhere [35], salinity and temperature are the major controls to the activity of SRM, methanogens and acetogens. As such, main inputs for this screening are salinity and temperature values. A temperature gradient of 30 °C/km was considered to estimate the temperature of the reservoirs [57].

### 3. Results and discussion

#### 3.1. Abiotic calcite dissolution due to hydrogen storage

Fig. 2A indicates that for the four formation brine compositions listed in Table 1 and at temperatures in the range of 40–180 °C, the calcite saturation index is equal to or above zero and therefore calcite is not expected to dissolve. Our evaluation does not consider temperature changes and mixing induced by flow, requiring confirmation of our results by reservoir models.

#### 3.2. Effects of methanogenesis and acetogenesis in hydrogen storage

For a formation brine with a low sulfate concentration (type 1) only methanogenesis and acetogenesis are likely to significantly influence hydrogen storage. For the best case scenario that does not consider indirect temperature effects, hydrogen loss due to methanogenesis is not significant and stays below around 0.6% per year (Fig. 3A). However, hydrogen loss by methanogenesis is slightly temperature dependent: The final hydrogen loss at $t = 10$ years increases from 3.4% to 5.9% by a temperature increase from 50 °C to 100 °C and then decreases to 5% by a further 22 °C increase in temperature (Fig. 3A). The temperature dependency of methanogenesis is due to the temperature effect on the total solubility of DIC species and the solubility of calcite and brucite (Mg(OH)$_2$). Our best case methanogenic hydrogen consumption is in agreement with hydrogen losses of ~3% by methanogens in Lehen, Austria [58].

Methanogenesis causes an increase in pH (Fig. 3C), due to the proton consumption in the process (reaction b), as observed previously [59]. Initially, methanogenesis is faster at 50 °C than the other simulated temperatures because of a higher solubility of DIC species (Fig. 3D). However, the higher methanogenesis rate leads to a higher pH that is self-inhibiting due the growth constraints on methanogenic activity. At higher temperatures, brucite precipitation (Fig. 3F) reduces the increase in pH due to common ion effect [60], and as a result, the methanogenesis rate at 75 and 100 °C becomes higher than that at 50 °C. At 122 °C, the negative effect of the low DIC species solubility on methanogenesis dominates the positive effect of higher buffering by brucite precipitation, resulting in a lower hydrogen loss than that at 75 °C and 100 °C.

Fig. 4A shows that in a worst case scenario (using the highest methanogenesis rates reported), a complete hydrogen loss is achieved in 3.5 to 5 years. Because methane is an energy carrier, the energy loss by methanogenesis is 27% of hydrogen energy (Fig. 4B). Temperature influences the rate of hydrogen loss via the two kinetic coefficients $\gamma$ and $C_A/(C_A + K_A)$. The higher the temperature, the lower the $C_A/(C_A + K_A)$ ratio, due to a lower solubility of DIC species, and the lower $r_i$. However, with an increase in temperature, the solubility of portlandite decreases [61], i.e. portlandite precipitates and buffers the environment in a lower pH (causing a higher $r$). With an increase in temperature up to 100 °C, the increase in $r$ dominates the reduction in the solubility of DIC species. By increasing temperature further to 122 °C, the adverse impact of the reduction of the concentration of DIC species on methanogenesis rate is stronger than the impact of increase in $r$. This change in the relative impact of $r$ and the solubility of DIC species explains the increase in the methanogenesis rate from 50 to 100 °C, and its decrease from 100 to 122 °C. It is noteworthy that in the best case scenario portlandite does not precipitate as the pH stays below nine throughout the simulation.
\( \gamma = 0 \) for \( pH_{\text{max}} = 9 \), and therefore the amount of brucite precipitation at different temperatures controls the differences in the methanogenesis rates, whereas in the worst case scenario, \( pH \) can become higher than nine \(( pH_{\text{max}} = 9 \), and as there are limited \( Mg^{2+} \) ions in the system, the effect of brucite precipitation is negligible. Therefore, one can conclude that if the methanogens in the system require \( pH \) below nine to survive, then the presence of \( Mg^{2+} \) in the formation brine can determine whether methanogenesis will happen or not. Fig. 4F shows that for the worst case scenario, calcite dissolution, brucite and portlandite precipitation have a negligible effect on the total porosity (max 2% reduction). Despite insignificant overall porosity change, local precipitation in pore throats (not simulated) could still influence permeability significantly [62].

Hydrogen loss due to acetogenesis in the best case scenario (Fig. 5A) is around 4% lower than the loss by methanogenesis (Fig. 3A) because acetogenesis is thermodynamically less favorable than methanogenesis \( (\Delta G^0 = -26.1 \text{ kJ/mol} \ H_2 \text{ for acetogenesis versus } \Delta G^0 = -33.9 \text{ kJ/mol} \ H_2 \text{ for methanogenesis [31]}) \), and therefore acetogenesis has a lower biomass yield (0.02 instead of 0.03, see reactions b and c). Despite a lower hydrogen loss, acetogenesis causes around the same energy loss as methanogenesis since the product of acetogenesis, acetate, is not an energy carrier. Calcite dissolution due to acetogenesis is around 50 mM higher than that of methanogenesis (Fig. 5E). The higher dissolution of calcite by acetogenesis is due to higher consumption of DIC species by acetogenesis (see reactions b and c, acetogenesis consumes around two times more \( HCO_3^- \) than methanogenesis, therefore, if methanogenesis and acetogenesis would proceed at
equal rates, the rates of calcite dissolution and portlandite precipitation under acetogenesis would be approximately twice the observed rates under methanogenesis).

For the worst case scenario, hydrogen loss due to acetogenesis is around 2.4 to 5.2% per year depending on the temperature (Fig. 6A), which is around 8 and 6 times less than that of methanogenesis at 50 and 100 °C, respectively. While a part of the lower hydrogen loss under acetogenesis relative to methanogenesis is because of the difference in the growth yield, another reason is that (for the worst case scenario) maximum specific growth rate for acetogenesis is 1.9 day\(^{-1}\) which is smaller than that of methanogenesis (4.1 day\(^{-1}\)). The slower worst case acetogenesis rate leads to a lower calcite dissolution (Fig. 6C) compared to that of methanogenesis (Fig. 4C). Even though calcite dissolution in acetogenesis is less than that of methanogenesis, the rock porosity reduction of acetogenesis is bigger (maximum 2.5%, Fig. 6F) compared to that of methanogenesis (1.2%). In methanogenesis, for each mole of bicarbonate, a mole of H\(^+\) is consumed (reaction b). Therefore, for each mole of calcite dissolved, a mole of portlandite precipitates. However,
for acetogenesis (reaction c), for each mole of bicarbonate, only around 0.5 mol of H⁺ is consumed. As a result, for each mole of calcite dissolved, only 0.5 mol of portlandite precipitates. This higher relative dissolution of calcite to precipitation of portlandite leads to the higher porosity change of acetogenesis compared to that of methanogenesis.

Our simulations neglected the limitation of essential nutrients such as N and P. Danish Technological Institute (2011) [43] showed that chalk dissolution leads to PO₄⁻⁻ as N and P. Danish Technological Institute (2011) [43] showed that change of acetogenesis compared to that of methanogenesis.

of calcite to precipitation of portlandite leads to the higher porosity

significantly lower, since subsurface microbes grow 10⁻⁶ times slower than those in nutrient rich growth media, have lag phases that last months to years compared to minutes to hours lag phases observed under laboratory conditions. However, the field observation at the Lobodice town gas storage site, where 17 % of the injected hydrogen was lost due to methanogenesis over a time span of seven months (30% loss per year) [67,68], shows that the maximum theoretical hydrogen loss rate calculated in this work can be experienced in field applications. This suggests that representative biochemical models are vital to assess the risk associated with a given hydrogen storage project.

Note that the simulated hydrogen loss values (\(loss_{simulation}\)) are corresponding to a given simulation time (\(t_{simulation}\)). However, assuming that hydrogen loss has a linear time dependence, one can estimate the hydrogen loss of a short hydrogen storage cycle \(loss_{cycle}\), and cumulative hydrogen loss of multiple storage cycles \(loss_{cumulative}\) through the following relationships:

\[
loss_{cycle} = \frac{t_{cycle}}{t_{simulation}} \times loss_{cumulative} \tag{3}
\]

\[
loss_{cumulative} = \sum_{i=1}^{n} \frac{t_{cycle}}{t_{simulation}} \times loss_{cumulative} \tag{4}
\]

where \(cycle\) is the time of a hydrogen storage cycle in year. Note that the \(loss_{cumulative}\) values reported in this work are based on initial storage pressure of 351 bar and temperatures considered in this work. Therefore, corrections have to be made when estimating hydrogen loss in other pressures and temperatures.

3.3. Simultaneous hydrogen storage-CO₂ storage in chalk reservoirs

Here we assess if simultaneous injection of CO₂ with hydrogen could inhibit calcite dissolution by methanogenesis such that the produced methane (due to methanogenesis) could be CO₂ neutral. To this aim we conduct the same simulation as for the methanogenesis worst case scenario at 75°C (dotted lines in Fig. 4) with the only difference being the substitution of 20% of hydrogen with CO₂. The gas composition of 80% hydrogen/20% CO₂ was chosen in accordance with reaction b, i.e. for each mole of hydrogen, 0.264 mol of CO₂ are required. Fig. 8A shows that injection of CO₂ with hydrogen (for the worst case scenario) speeds up methanogenesis such that the time required for complete conversion of hydrogen into methane is reduced from 3.6 years to 2.25 months (Fig. 4A). This increase in methanogenesis rate is because the dissolution of the added CO₂ increases C(4 +) concentration by three orders of magnitude (compare Fig. 8B and 5G). Co-injection of CO₂ also reduces calcite dissolution from around 4 M under pure hydrogen (Fig. 3C) to around 0.02 M (Fig. 8C). Note that the part of calcite dissolution curve with a negative slope demonstrates precipitation. Coincidence of calcite precipitation with CO₂ depletion (Fig. 8D) proves that the calcite dissolution shown in Fig. 8C is solely because of CO₂ injection and not methanogenesis, i.e. partially supplementing hydrogen with CO₂ can lead to CO₂ neutral methane production. It is worth mentioning that the CO₂/hydrogen ratio that was considered in our simulation is based on fast methanogenesis rates that will cause complete hydrogen loss within
Fig. 7. Critical salinity versus critical temperature for A) sulfur species reducing microorganisms, B) methanogens and C) acetogens. Circle markers show the experimental observations collected by Thaysen et al. (2021) [82]. The dashed line lines have been created by polynomial regression of the boundary data points and define the critical salinity/temperature boundary out of which the corresponding metabolisms have not been observed to occur. D-E) Salinity vs temperature for various Danish North Sea chalk hydrocarbon reservoirs plotted together with the critical temperature salinity line derived in A-C. Fields that fall out of the red dashed line are not likely to experience hydrogen loss due to the corresponding metabolism. Circle markers show fields that are susceptible to all three metabolisms. Other markers show fields in which at least one metabolism is not likely to occur. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. Effects of methanogenesis in a chalk reservoir with formation brine type 1 (negligible sulfate content) at 351 bar and 75° C after simultaneous hydrogen (80%)-CO₂(20%) storage. A) Hydrogen loss, B) changes in the sum of concentration of DIC species, C) calcite dissolution, D) CO₂ concentration in the gas phase.
the storage period. Lower methanogenesis rates causing partial hydrogen loss will require less CO₂ so as to make sure that the injected CO₂ is converted to methane before production. When the high purity of hydrogen is important, in the light of our results, it is clear that the use of CO₂ as a cushion gas for hydrogen storage is not advisable as it clearly speeds up hydrogen bioconversion through methanogenesis by several orders of magnitude.

3.4. Sulfate reduction

Fig. 9A depicts that souring can cause an insignificant hydrogen loss of about 0.5%. The produced H₂S concentration (1015 ppm; Fig. 9B) is higher than what is typically observed in a reservoir souring process (below 200 ppm) [69–71], but occurs only in the early stage of hydrogen storage. This higher concentration of H₂S is because SRM can utilize hydrogen faster than organic electron donors available in a reservoir souring process. The reason for the small hydrogen loss and the onset of the H₂S production is that our model considers a limited sulfate concentration of 1250 mg/L in the formation fluid. In a real chalk reservoir system, nutrients are likely to at least partly be replenished by inflowing brine and mineral weathering (e.g. anhydrite, or sulfate minerals). Our results are in line with reported hydrogen losses of 2–4 % by sulfate reducers at the hydrogen storage test site in Ketzin, Germany [72], considering correspondingly higher sulfate concentrations of 3800 mg/L and no nutrient replenishment in our model.

The density of H₂S (1.36 g/L) is 15 times higher than density of hydrogen (0.090 g/L), causing a separation between the two gases which may reduce the H₂S concentration in the produced hydrogen if the well completion is located at the top of the reservoir. The impact of souring on mineral precipitation and porosity was negligible (not shown).

3.5. Screening of Danish North Sea chalk hydrocarbon fields for hydrogen storage

Fig. 7D to F show the temperature/salinity condition of various chalk hydrocarbon fields in the Danish sector of the North Sea. Dagmar, Skjold, Halfdan, Dan, Tyra, Valdemar and Roar have relatively low temperatures and salinities of below 80 ºC and 1 M NaCl, respectively, making them susceptible for methanogenesis, acetogenesis and souring. Among these reservoirs Halfdan, Dan, Dagmar and Skjold may experience significant H₂S production as they contain high sulfate concentrations (592–1250 mg/L). Tyra and Roar have low salinities of 0.547 M NaCl and temperatures of 68 ºC and 71 ºC, respectively, that support methanogenesis. Therefore, a maximum energy loss of around 27% could occur and these fields are not recommended for pure hydrogen storage. However, an optimum fraction of 20% CO₂ could be co-injected with hydrogen in these reservoirs to produce carbon neutral methane. Ragnar, Kraka, Gorm are only susceptible to souring as they contain significant sulfate concentrations of 592 mg/L. Depending on how significant the increase in capital and production costs is due to a short period of H₂S production, these reservoirs may be considered as potential candidates for hydrogen storage. Rolf, Svend, Harald west and South Arne have high reservoir temperatures of above 95 ºC and salinities of above 1.4 M NaCl. According to Fig. 7D to F there is a low risk for microbial reactions in these reservoirs, favoring their use as hydrogen storage sites from the microbial point of view.

3.6. Caveats and future directions

This study determines the feasibility of hydrogen storage in chalk reservoirs without consideration of fluid flow and mixing (batch-scale). Such batch-scale feasibility is necessary for a successful storage project, but it is not sufficient. Future experimental effort is required to understand the impact of hydrogen storage on permeability of chalk (examples for sandstone reservoirs can be found in [73]). Such experimental studies together with wettability [74,75] and /relative-permeability studies [76] can be coupled to the results produced here through reactive transport models in order to understand the impact of mixing on the process.

4. Conclusion

Hydrogen storage can influence/be influenced by chalk reservoirs only through biotic reactions. Methanogenesis, acetogenesis and souring are the main microbial risks for hydrogen storage in chalk. The effects of methanogenesis and acetogenesis on hydrogen storage in a chalk reservoir can be insignificant given possible slow growth kinetics of methanogens and acetogens. However, high methanogenesis and acetogenesis rates are theoretically possible if (i) the maximum specific growth rate of the indigenous methanogens/acetogens approaches the maximum specific growth rate of the fastest growing methanogens/acetogens observed in the labs, and (ii) the maximum pH tolerable by indigenous methanogens is above 10. Temperature can influence the rate of hydrogen loss by methanogenesis and acetogenesis as it controls DIC concentration as well as pH. Co-injection of CO₂ with hydrogen can inhibit calcite dissolution and produce carbon neutral methane. The presence of sulfate can trigger souring that can increase hydrogen

Fig. 9. A) Hydrogen loss and B) H₂S production due to souring in a depleted hydrocarbon reservoir with the formation fluid of type 4 (with a limited concentration of sulfate of 1250 mg/L).
storage costs and compromise safety due to the corrosive and toxic nature of H₂S. According to our results we expect souring to be an initial, short term problem, only, as sulphate availability is largely restricted to a (limited) formation brine sulphate content. Many of the Danish North Sea chalk reservoirs are therefore good candidates for future hydrogen storage considering the studied risks.

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CRedit author contribution statement

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

[40] Wolery TJ. EQ3NR, a computer program for geochemical aqueous speciation-solubility calculations: theoretical manual, users guide, and related documentation (Version 7.0); Part 3, Lawrence Livermore National Lab.(LLNL), Livermore, CA (United States); 1992.