Hydrogen Storage in Saline Aquifers — On the Efficiency of CH_4, CO_2 and N_2 as a Cushion Gas?

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Abstract
Hydrogen as a major energy vector plays an important role in the decarbonization of heavy industry. However, intermittency and sessional availability of renewable energy sources, as well as the demand for energy at different times and places, require a medium- to long-term storage technology. Underground hydrogen storage in saline aquifers could be a good option given the storage capacity and availability of aquifers in different geological settings. However, saline aquifers may suffer from many operational, geological, and geochemical complications. In this paper, we attempted to evaluate the need of cushion gas (nitrogen, methane, and carbon dioxide) on the success of hydrogen storage in saline aquifers. Hydrogen storage in the saline aquifer can be simulated through CMG software. There are relevant features which are present in the simulator for the hydrogen storage. WINPROP-CMG is the compositional software which works on the basis of EOS (equation of state). The results obtained from simulating a realistic reservoir model indicated that that carbon dioxide and methane injection both were outperformed than nitrogen in terms of water displacement, cumulative injection and production. Considering the certain operational and economic aspects, injection and production cyclic mode provided the acceptable remaining gas volume and cumulative gas compared to the cushion gas scenarios, therefore, cyclic gas injection would be a promising approach to overcome the gas contamination issue.

Keywords: Hydrogen, geological storage, aquifers, cushion gas, cyclic injection

1. Introduction

Hydrogen as a significant energy vector plays a major role in decarbonizing the heavy industry and unlocking a sustainable energy future. However, green hydrogen production through electrolysis requires a large (Gigaton) storage site due to the intermittency of wind and solar-energies (Rodrigues et al. 2014, Braff et al. 2016, Carriveau and David. Ting 2016, Heinemann et al. 2021). Given the fact that surface facilities (e.g., pipelines or tanks) have limited storage capacity (Beckingham and Winningham 2019), saline aquifers offer quality sites for storage capacity. In fact, there have been some pilot projects in the Czech Republic and France where hydrogen have been stored in saline aquifers (Carden and Paterson 1979, Foh et al. 1979, Lord 2009).

Cushion gases such as nitrogen and methane are denser than hydrogen, can improve pressure management within the aquifer and have better sweep efficiency than hydrogen to reduce migration of water towards the production well during production (Raza et al. 2022). Depending on depth and required operating pressure, the amount of cushion gas in a storage site can vary from 20% to up to 25% of the total volume available for storage (Zivar et al. 2021). The ability to change surface wettability, to produce significant density differences, cost and ease of migration in porous media are some of the criteria for selecting a cushion gas (Heinemann et al. 2021). However, cushion gas may interact with hydrogen (mixing, dispersion, and dilution) and porous media (phase trapping) (Pfeiffer et al., 2017). For example, CO_2 is one of the potential cushion gases that can alter surface wettability for better hydrogen storage in saline aquifers. It also has a higher molecular weight than nitrogen and methane, can reduce water production and can be stored in saline aquifers at the same time, as observed by the good experiences of the Sleipner (North Sea), Snøhvit (Barents Sea) and In Salah (Algeria) projects (Aminu et al. 2017). However, the application of CO_2 as an effective cushion gas for hydrogen storage in saline aquifers must be carefully analysed.

In this paper, an attempt was made to provide a deeper insight into the potential of hydrogen storage in saline aquifers. A real aquifer was simulated using the CMG software and the effect of cyclic injection and cushion gases was evaluated compared to single cycle injection mode.

2. Methodology

Hydrogen storage in the saline aquifer can be simulated through CMG software. WINPROP-CMG is the compositional software which works on the basis of EOS (equation of state). Characterization of fluid, matching of fluid model with the data of laboratory from the implementation of regression, simulation of processes which incorporate calculations of multiple contact miscibility, solubility of light weight gases in fluid like water or brine and generation of fluid model for CMG simulators are the featured capabilities which exist in WINPROP-CMG. Phase behaviour and generation of properties associated with the component can be analyzed and calculated from the WINPROP-CMG which would support the modeling for the compositional simulator of CMG-GEM. CMG-GEM actuates as an EOS simulator through which simulation of mechanisms involved in the underground hydrogen storage can be done. Gas solubility in aqueous phase is the key process because of hydrogen injection in saline aquifer. Hydrogen solubility in brine depends on Henry's law. The governing equation of Henry's Law for the utility in the simulation of underground hydrogen storage is;

$$f_{H_2\,(Gas)} = f_{H_2(Aqueous)} = W_{H_2} * \text{Henry-Constant}_{H_2} \quad (1)$$

Where $f_{H_2(Gas)}$ and $f_{H_2(Aqueous)}$ are the fugacities of hydrogen in gas and aqueous phase respectively. W_{H_2} represents hydrogen's mole fraction in the aqueous phase. Henry's constant for hydrogen is the function of pressure however it depends on pressure, temperature and salinity for methane, carbon dioxide and nitrogen. For the study of hydrogen storage, definite methods for the calculation of density and viscosity of aqueous phase are present in the simulator. The aqueous phase density can be calculated from the two methods i.e., Linear and Rowe-Chou where first method works as a linear function of pressure. The aqueous phase viscosity can be considered and calculated through three approaches. For fluid modeling, aqueous phase viscosity is taken as constant, as a function of pressure, temperature and salinity or as a function of pressure, temperature, salinity, polymer concentration and shear effect. Density and viscosity of gas phase can be measured from Peng-Robinson EOS and Jossi, Stiel and Thodos correlation respectively. Additionally, CMG-GEM can incorporate the vaporization of water during the gas injectivity for the development of model. The injectivity of gas can be affected by the vaporization of water. The equation for water vaporization defines the equality of fugacities of water in the gas and aqueous phase is;

$$g_{n_c} = f_{H_2O_{(Gas)}} - f_{H_2O_{(Aqueous)}} = 0 \qquad (2)$$

Where $f_{H_2O_{(Gas)}}$ and $f_{H_2O_{(Aqueous)}}$ are the fugacities of water component in gas and aqueous phase. Equation (2) describes the thermodynamic equilibrium between the gas and aqueous phase.
The simulation of this study was carried out using the CMG-GEM simulator, which works on the basis of the equation of state according to the compositional model. The simulator assumes the mechanisms that may occur during underground hydrogen storage. An infinite-acting aquifer model was created for several cycles of hydrogen injection and production. The dimension of the aquifer was 180 m × 180 m with a thickness of 15 m. The rock properties (i.e., porosity and permeability) of five layers of fluvial sand and shale were considered in the model. Figure 1 represents the model which is created for the purpose of this study. The model was brought to static equilibrium by assuming an initial aquifer pressure of 6400 kPa at a depth of 2342m. The model was 100% saturated with water at the start of the simulation and contained no dissolved gas. The three main directions of the model were evenly meshed with 19 cells in the x-direction, 28 cells in the y-direction and 5 cells in the z-direction. The data set of input parameters used for the static model of the aquifer is given in Table 1.

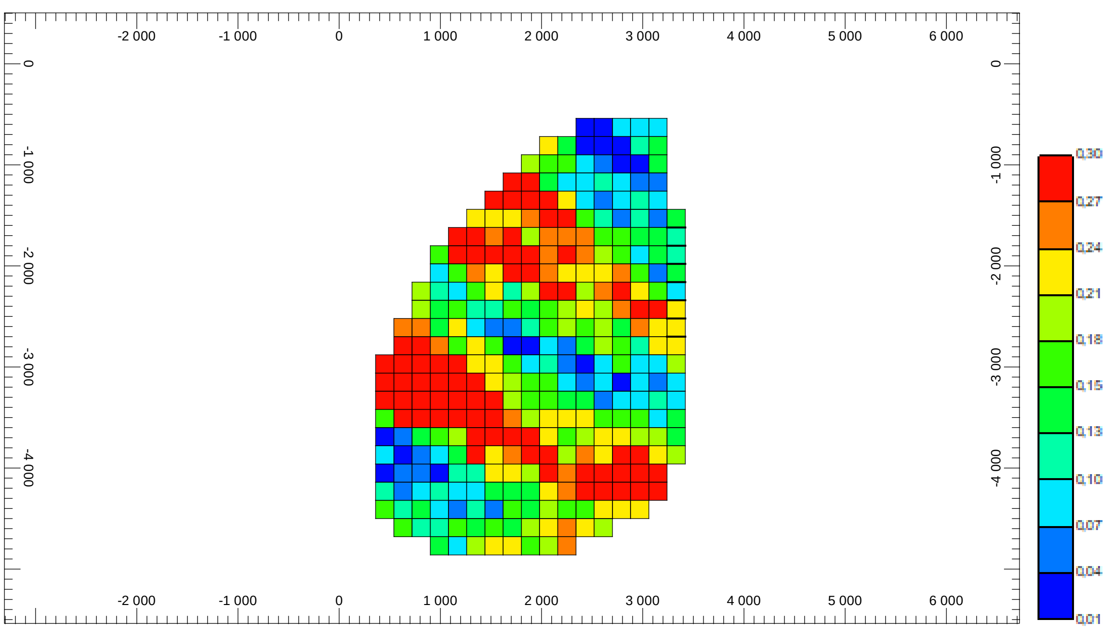

Figure 1: Variation of the porosity in the base aquifer model used in this study
An injection well was considered in the middle of the aquifer at a depth of 2400 metres having only the resident brine in the pore spaces. Different scenarios were considered, such as pure hydrogen injection and production (base case), cyclic gas injection, water monitoring, cushion gas injection and potential methanation. PVT Modelling of the fluids was carried out using the

WINPROP-CMG considering the Peng-Robinson equation of state, while the solubility of the brine was calculated using Henry's Law correlation at 50 ^{o}C. Molecular diffusion was introduced at the beginning of the injection to create a diffusive flow with respect to the liquid mole fraction. Hypothetical relative permeability data along with hysteresis were also considered to include the solubility trapping of the gas. Henry's law was used to evaluate the gas solubility based on the variation of pressure, temperature, and salinity. The density and viscosity of the aqueous phase were also considered in the simulation. The density of the aqueous phase was calculated using the Rowe-Chou method, while the viscosity of the aqueous phase was calculated from Kestin el al. correlation as a function of pressure, temperature, and salinity. Figure 2 shows the relative permeability curves used in the simulation.

In the modelling, a base case was developed for single cycle and the gas injection and production rates were 1358 m^3/day for 6 months and 2717 m^3/day for 3 months, respectively. In the cyclic injection case, the injection started with 6 months (184 days) of injection and 3 months (90 days) of production. This cycle was repeated five times for five years. Cyclic gas injection for hydrogen storage was carried out at gas injection and production rates of 1358 m^3/day and 2717 m^3/day, respectively. Different scenarios of cushion gas injection with N_2, CH_4 and CO_2 were considered where nitrogen and methane were not water soluble. In the case of N_2 injection, the injection rate of nitrogen was 3000 m^3/day for 6 months, while H_2 injection and production rates were 1358 m^3/day for 6 months and 2717 m^3/day for three months in five cyclic. In carbon dioxide and methane cases, injection of CO_2 or CH_4 was made for 12 months at a rate of 1500 m^3/day then H_2 was injected and produced at a rate of 1358 m^3/day for six months and 2717 m^3/day for three months, respectively, in five cycles. It is known that methanation can take place in the presence of microbial activity in a hydrogen storage site (Strobel et al. 2020). However, according to Thaysen et al., (2021), the methanogenesis process ($1/4HCO_3^- + H_2 + 1/4H^+ = 1/4\ CH_4 + ¾\ H_2O$) is inhibited by high temperature, high salinity and high pressure conditions (Thaysen et al. 2021). Given the parameters given in Table 1, it was assumed that methanation will not occur in the saline aquifer. Tables 2 and 3 give the properties of hydrogen and its binary interaction coefficient with cushion gases.

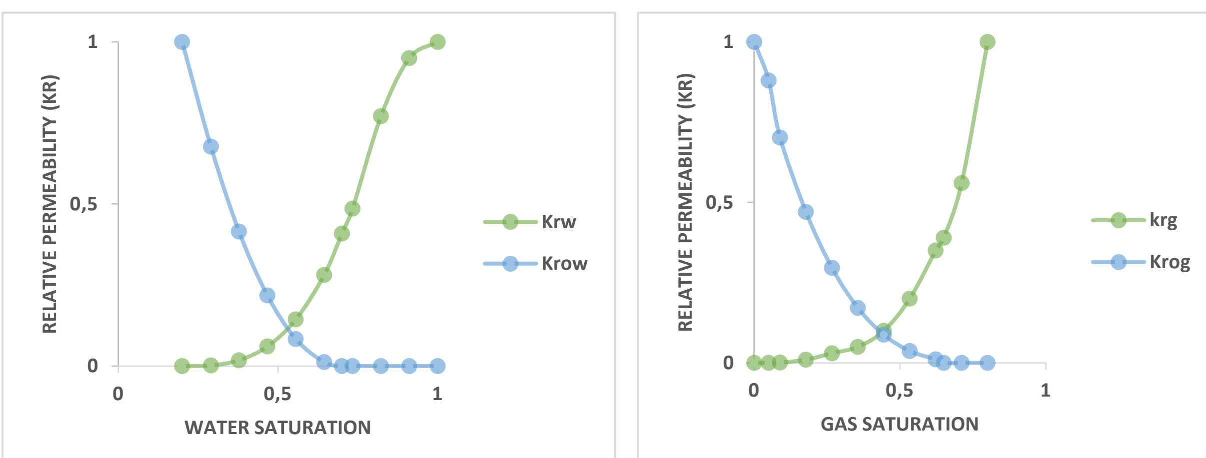

Figure 2. Relative permeability function of H_2-H_2O system

Table 1. Basic input parameters used for the modeling of the saline aquifer

Parameters	Value
Grid blocks	2660
Length	180 m
Width	180 m
Equilibrium Depth	2342 m
No of injection and production well	1
Average porosity	20%
Average permeability	100 mD
Top depth	2300 m
Average reservoir thickness	15 m
Initial pressure	25 MPa
Initial temperature	80°C
pH	5
Water compressibility	4.6E-7 1/kPa
Hysteresis	0.3
Salinity	10wt%

Table 2: Properties of hydrogen used in this study

Critical Pressure P_c	Critical Temperature T_c	Acentric Factor	Molecular Weight MW	Specific Gravity	T_b	Compressibility Factor Z (Rackett)	Critical Volume V_c	Parachor
atm	K		g/gmol		°C		L/mol	
12.98	33.18	-0.214	2.0159	0.07107	-252.76	0.31997	0.066952	31

Table 3: Interaction coefficients of hydrogen with cushion gases considered in this study

Binary Interaction Coefficients	CO_2	N_2	CH_4
H_2	-0.1622	0	0.0156

In this study, three different cases were adopted for the analysis of hydrogen storage in saline aquifers: i) gas injection with no cycles (base case), ii) gas injection in five cycles iii) cushion gas injection. It was also assumed that none of these cases could cause thermal shocks or changes in the overall behaviour of the storage site.

3. Results and Discussions

Different scenarios of hydrogen injection and production from a saline aquifer are presented here. The effect of gas injection with no cycle, cyclic gas injection and cushion gas methanation were investigated with effective factors participating.

The comparison is made for all cases to evaluate the best scenario. The comparison of results for the base case, cyclic gas injection, nitrogen, CH_4 and CO_2 injection cushion gas is shown in Figure 1. From this figure, it can be seen that the injection rate remains the same for all cases. However, the gas rate for the nitrogen cushion gas decreased in the early stages of certain cycles, as explained earlier. Figure 2 shows the cumulative gas during injection and production. It appears that CO_2 and methane injection provides same and the highest cumulative production. It also appears that nitrogen may not be the best choice as a cushion gas for hydrogen production.

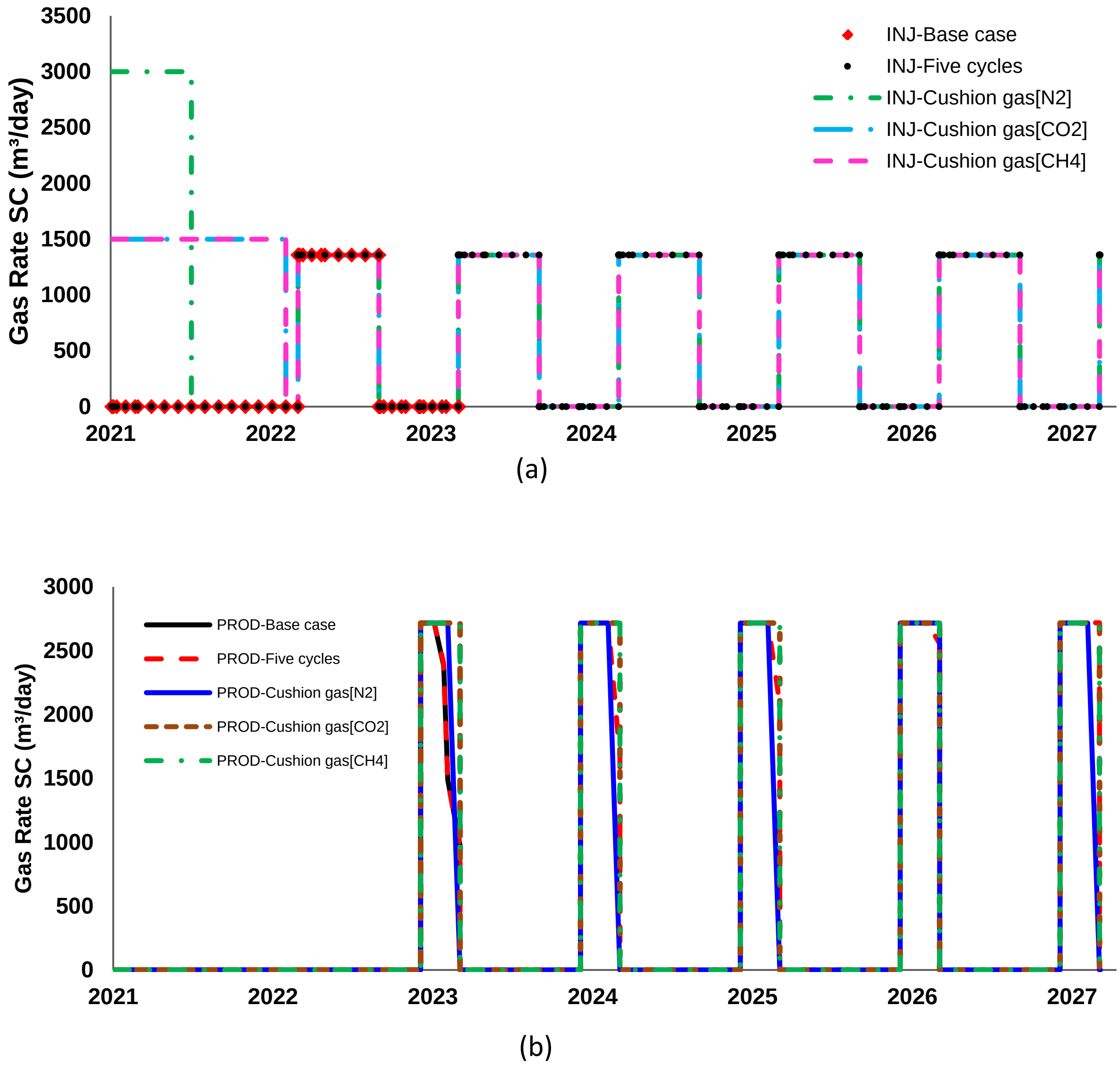

Figure 1: Gas rates during (a) injection and (b) production

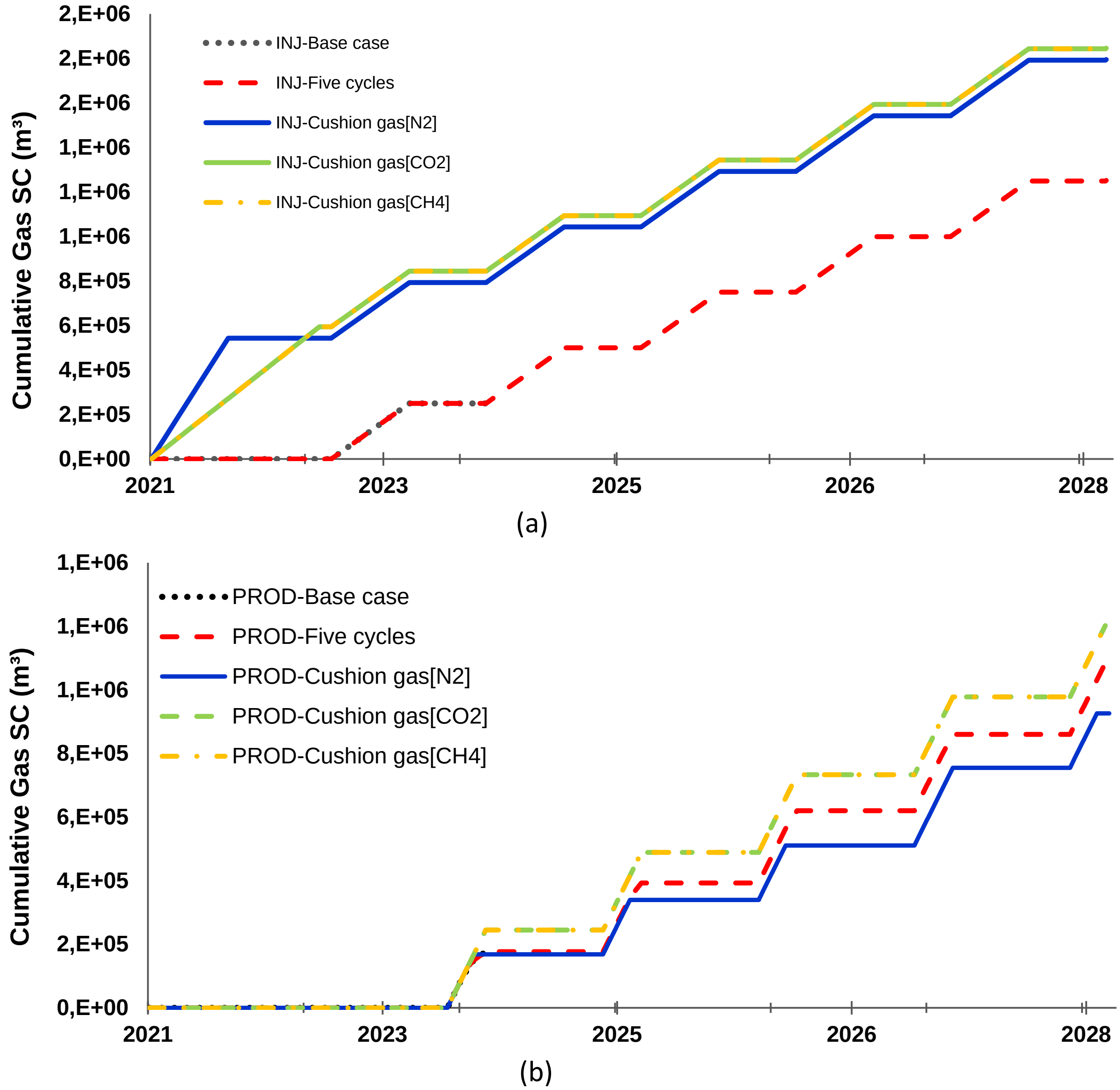

Figure 2: Cumulative gas during (a) injection and (b) production

Water production shows comparatively high rates for the base case and cyclic gas injection (see Figure 3). Nitrogen, CH_4 and CO_2 can reduce water production and bring it to minimum rate. As such, N_2 >CO_2>CH_4 can be ranked to provide systematic water production with cycles along with pressure maintenance, however, H_2 production is not feasible (see Figure 2). Water production for methane injection provides high rates for initial cycles. It was also shown that the water rate decreases if only five cycle mode is considered without cushion gas injection.

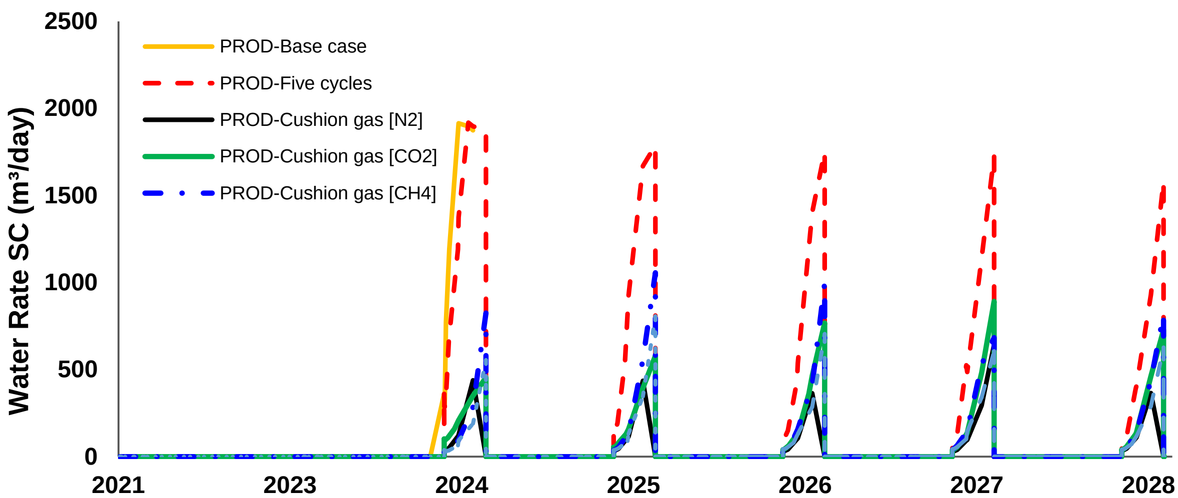

Figure 3: Water production rates

The volume of gas injected and produced in different scenarios simulated in this study is reported in Table 4 along with percent increase of gas (injected, produced and remaining) compared to the base case. From the table, the base case has the least amount of gas in the reservoir but suffers from significant water production compared to the other cases. In addition, in the cyclic gas injection, provide the acceptable remaining gas volume and cumulative gas compared to the cushion gas scenario, while the remaining gas volume is lower compared to the cushion gas scenarios. Therefore, cyclic gas injection would be a promising approach. The volume in the case of cushion gas injection provides a high level of remaining gas. In the case of cushion gas, it seems that CO_2 and CH_4 would be a much better approach for hydrogen storage due to the high gas production rate, lower water production and high cumulative hydrogen production. Compared to the base case (single cycle), cyclic injection mode offered 400% increase in injected gas, 541% increase in produced gas and 100% increase in remaining gas and thus can be preferred over cushion gas mode

Table 4: Differences in the volume of gas produced at the end of simulation in 2028

Sr. No.	**Cases**	**Cumulative Gas (Injected), ×10^6 m^3**	**Cumulative Gas (Produced), ×10^6 m^3**	**Remaining gas in reservoir, ×10^6 m^3**
1	Base Case [Single cycle]	0.25	0.17	0.08
2	Five Cycle Injection	1.25 (↑400%)	1.09 (↑541%)	0.16 ((↑100%)
3	Cushion Gas: N_2	1.79 (↑616%)	0.92 (↑441%)	0.87 (↑988%)
4	Cushion Gas: CO_2	1.84 (↑636%)	1.22 (↑618%)	0.62 (↑675%)
	Cushion Gas: CH_4	1.89 (↑656%)	1.22 (↑618%)	0.62 (↑675%)

It should be noted, however, that the injection of CO_2 for geological storage imposes significant costs on the installation system to transport liquid or supercritical CO_2, which is known for its corrosive behaviour. As shown in this paper, there may also be a large amount of CO_2 produced that needs to be captured at the well site. This is another complexity and cost involved in such projects. In light of these experiences, further studies are needed to clarify the economic and scientific feasibility of injecting (storing) CO_2 as well as improvement in the residual amount of CO_2 in hydrogen storage sites.

4. Conclusions

In this work, hydrogen storage in saline aquifers was simulated in three different scenarios. It was shown that a shorter time interval between injection and production ensures a higher recovery of hydrogen. Introducing cycles for injection and production reduces the water rate and improves recovery. It seems that nitrogen as a cushion gas does not lead to efficient hydrogen production. However, CO_2 and CH_4 as a cushion gas could offer the same and highest recovery of injected hydrogen with high cumulative gas production at lower water production. Methane, on the other hand, is also a good choice as it can reduce the water production and improve the hydrogen production after injection.

There are certain operational and economic aspects that need to be evaluated before considering carbon dioxide and methane as an effective cushion gas for hydrogen storage. Injection and production cyclic mode provide the acceptable remaining gas volume and cumulative gas compared to the cushion gas scenarios, therefore, cyclic gas injection would be a promising approach to overcome the gas contamination issue.

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