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Abstract

This presentation summarizes the theoretical results of a model that predicts the impurities during underground hydrogen storage due to microbial sulphate-reduction.

Typically, one of the critical aspects of hydrogen storage operations, focusing on safety and an economic perspective, is the purity of hydrogen after withdrawal from subsurface storage. The aim is to deliver the same purity of stored hydrogen as injected, preferably without any additional surface treatment. A theoretical contamination of the gaseous hydrogen is due to the activity of microbes living in the brine-filled sump of the cavern. During the leaching phase of the cavern, the microbes are transported into the cavern by fresh water injection. Hereby, various microbial species may be present and active during operation, namely methanogens and sulphate-reducers. Further, the dissolution of carbon dioxide into the brine-filled sump and the gas could lead to additional contamination.
All in all, the model demonstrates the capability to predict the possible microbial contamination of stored pure hydrogen. Following the hydrogen withdrawal during the operation of a pilot cavern, the prediction model will be calibrated with real test data. Further, the model is adaptable to other microbial reactions for future studies.

Key words: underground hydrogen storage, salt caverns, impurities modeling, hydrogen contamination

1. Introduction

Hydrogen provides one of the key technological solutions for Europe to reach its climate targets and become the first climate-neutral continent by 2050 (Zapf 2017). Typical fluctuations, particularly those caused by green hydrogen generation, require subsurface energy storage in caverns or porous rocks to structure the demand and ensure the security of supply. Several projects are underway to prove and investigate the technology for underground hydrogen storage in salt caverns in detail. Among other projects, the storage aspects of high-purity hydrogen are being tested in the hydrogen pilot cavern (Uniper 2024).

The primary field test focuses on the technical and economic feasibility of storing hydrogen underground with high purity for long-term storage. The pilot project includes extensive testing of materials (completions) and the cavern itself. So far, the project performance demonstrates promising results for heading toward commercial storage operations (Uniper 2024).

A crucial aspect of operations, from both safety and economic perspectives, is maintaining the purity of hydrogen after its withdrawal from subsurface storage. The goal is to ensure that the hydrogen retains the same purity as when it was injected, ideally without requiring additional surface treatment. One potential source of contamination is microbial activity within the brine-filled sump of the cavern. During the leaching phase, microbes get into the cavern by fresh water injection, where various species, such as methanogens and sulfate-reducing bacteria, may become active. Additionally, the dissolution of carbon dioxide into the brine-filled sump and the gas itself could contribute to further contamination.

Experimental studies analyzing the brine show no active microbes. Nevertheless, the possible existence of microbes must be considered. A numerical prediction model has been established to investigate these processes. To conclude the risk of contamination, an existing 0-model was adapted to account for larger volumes of gas and water and sulfate reducer as the main microbial reactions. The model couples the growth and conversion of hydrogen to hydrogen-sulfide with the mass transfer of components between the brine and gas phases. A double-Monod model was implemented for microbial growth and conversion. A sensitivity analysis was performed on specific parameters. The yield coefficient and specific growth rate have the highest impact on microbial conversion. The results show the strong dependence of the mass transfer coefficient on possible hydrogen-sulfide contamination.

2. Modeling

The modeling is based on a previous development model from Strobel et al. (Strobel et al. 2023), which deals with converting methane in case of hydrogen and carbon dioxide exposure. The model is a 0-D model that handles the brine and gas phases. Microbes only live in the aqueous phase of the model, where sulfide is also present. In the gaseous phase, hydrogen is initially present, but hydrogen-sulfide occurs in the gas stream during simulation (Buzogany et al. 2023).

The central equation for the conversion of hydrogen in the model is the sulfate-reduction by microbes inside the aqueous phase. The equation can be expressed as follows:

$$SO_4 + 5H_2 = H_2S + 4\,H_20$$

Sulfate is reduced with hydrogen as a substrate for the microbes to hydrogen sulfide and water. As mentioned above, hydrogen sulfide is declared an impurity as it creates challenges for the operations and the economics of the storage scenarios. Assuming that most hydrogen molecules are present in the gas phase of the reactor, the conversion process would result in a reduction of molecules, leading to a corresponding decrease in gas-phase pressure.

The literature substitutes several models for microbial growth. Simple models do not include substrate limitation and inhibition factors (Chmiel 2011). In the model, there is no inhibition by tracer elements, but it is assumed that the environment with hydrogen (dissolved into the brine) and sulfate leads to substrate-limited conditions. Therefore, the double Monod model (Ebigbo, Golfier, and Quintard 2013) was used, which can be written as follows and describes the growth rate depending on two substrates:

$$\mu_{growth} = \mu_{growth}^{\max} * \left(\frac{C_{H_2},w}{\left(K_{H_2},w + C_{H_2},w\right)}\right) * \left(\frac{C_{SO_4}^2,w}{\left(K_{SO_4},w + C_{SO_4},w\right)}\right)$$

Where C_x are the moles concentrations of substrates in mol/m³ inside the water phase, K_x are the half-saturation constants of the two substrates in mol/m³, and $\mu_{growth}^{\max}$ is the maximal growth rate calculated based on the experiments during the exponential growth phase in 1/s. The half-saturation constant describes the concentration of the respective substrate where the growth rate reaches half of the maximal growth rate. The half-saturation constant and the maximum growth rate depend on the species and environmental conditions.

In the absence of one or more substrates, the microbes need to maintain their metabolism. Therefore, a decay/maintenance coefficient is required to describe this process:

$$\mu_{decay} = -b$$

where b is a constant decay and maintenance coefficient in 1/s.
As mentioned before and also seen in the figures of the experimental results, both microbial species have a lag phase (Wood, Ginn, and Dawson 1995). The lag phase is expressed by a piece-wise function (Wood et al. 1995):

$$\lambda = \begin{cases} 0, & if\ t < t_L \\ \dfrac{(t - t_L)}{(t_E - t_L)}, & if\ t_L \leq t \leq t_E \\ 1, & if\ t > t_E \end{cases}$$

Where t is the time of the experiment in s, starting with the first contact of the substrate with the liquid, and t_L (s) is the end of lag phase until no growth can be noticed in the experiment, and t_E (s) is the time when the exponential growth is reached in the experiments.

The microbial change in the liquid phase can be represented by combining the Monod model for microbial growth, the decay/maintenance model, and the piecewise function for the lag phase.

$$\frac{(dX_m)}{(dt)} = \mu_{growth}^{\max} * X_m * \lambda_{lag} * \left(\frac{C_{H_2},w}{(K_{H_2},w + C_{H_2},w)}\right) * \left(\frac{C_{SO_4},w}{(K_{SO_4},w + C_{SO_4},w)}\right) - b * X_m * \lambda_{lag}$$

where X is the total microbial number in the water phase in several cells, the number of microbes stays constant as long as the lag phase function is zero; the microbial number increases until one substrate is depleted, and the decay/maintenance term dominates.

To initialize the model, the initial thermodynamic equilibrium must be calculated. Further, the reduction and increase of the main components have to be considered. Unlike the microbial model, the compositional changes in the gas and water phases must also be considered. The concentration of elements in the water phase (solubility) is typically modeled using Henry's Law, expressed by the following equation (Sander 2015):

$$H_n = \frac{C_{\{w_n\}}}{p_{\{x_{\{gn\}}\}}}$$

where $C_{w,n}$ is the mol concentration of a component in the liquid phase, p_{xg} is the partial pressure of that component in the gas phase under equilibrium conditions in Pa and H_N is the Henry solubility constant at threshold temperature in mol/(m^3*Pa). To account for the higher temperature inside the reactor, the Henry constant can be corrected with the following approach:

$$H(T) = H^\circ * \exp\left[\frac{-\Delta sol \cdot H}{R} * (\frac{1}{T} - \frac{1}{T^\circ})\right]$$

- H(T) represents Henry's law constant at temperature T,
- H° is Henry's law constant at the reference temperature (T°),
- $-\Delta sol \cdot H$ is the enthalpy of dissolution,
- R is the universal gas constant,
- T is absolute temperatures in kelvin

The partial pressure of each component, which is required for the Henry Law, can be written as follows:

$$Px = \left(\frac{Ng_n}{Ng_t}\right) * PT$$

Where P_t is the total pressure of the gas mixture in Pa, Ng_n is the number of moles for one component in the gas phase, Ng_t is the sum of moles in the gas phase, and P_x is the partial pressure of the component required for Equation (X).

A fundamental assumption of Henry's law is that equilibrium exists between the concentrations of a given component in the gas and aqueous phases. While this assumption is held in the initial state within the reactor, it becomes invalid during microbial growth due to continuous consumption in the aqueous phase. To account for this dynamic, a mass-transfer model is employed to describe the flux of molecules across the phase boundary, driven by the concentration gradient. This model is based on the two-film theory, where the interfacial "film" represents resistance to mass transfer, governing the diffusion process between the gas and liquid phases.

Since no chemical reactions occur in the gas phase, the temporal change in the concentrations of the substrates, hydrogen and carbon dioxide, is primarily governed by mass transfer and can be expressed as follows:

$$\frac{dN_{H_{2g},SO_{4,g}\ \ ,CH_{4g}}}{dt} = -k_{g,w}\left(x_{H_{2l},SO_{4,l},CH_{4l}} - x_{H_{2li},SO_{4,li},CH_{4li}}\right)$$

Where $k_{g,x}$ is the mass transfer coefficient in *(mol/s)* for gas and water, which is equal for all components and *Ng* is the number of moles in the gas phase. The subscript *li* indicates the concentration in the liquid phase when it is in equilibrium with the gas phase.

To connect microbial biomass production with substrate consumption and product formation during sulfate-reducing metabolism, the yield coefficient is introduced. This coefficient represents the amount of biomass produced per mole of the respective component, with units of mol/mol .

The resulting equation set is equal to the one seen above but adds each component's Monod growth, decay, and yield coefficient. The equation system is implemented in Python, and the set of ordinary differential equations is solved by "odeint", which uses lsoda from the Fortran library odepack.

3. Initialization and Workflow

As the theory is quite theoretical, most of the parameters are chosen based on a literature review. The salt content of the brine was measured for the pilot cavern to be above 200 g/l, which excludes most of the microbes. Three species were found based on the study from (Thaysen 2021), and the growth rate, yield coefficient, and half-saturation constants were averaged. The complete volume of the cavern is known, as well as the desired gas/brine relation. The solubility and Henry coefficient were taken from (Sander 2015).

The following table summarizes the initial parameters:

PARAMETER	VALUE	COMMENT
V_T	3000 m^3	The total volume of the cavern
$P_{I,T}$	245 bar	Initial and total pressure
$T_{I,T}$	50 °C	Initial and total temperature inside the cavern
C_I	100% H_2	Initial concentration in the gas phase
U_{MAX}	5.38E-7 1/s	Maximum growth rate
Y_{H2}	1.5E12 mol/mol	Yield coefficient
K_{H2}	6.75E-10 mol	The half-saturation constant of H_2
K_{SO4}	3.06625E-08 mol	The half-saturation const of SO_4
A_{LAG}	1E6 s	Lag phase
B_{LAG}	1.5E6 s	Transition phase
T	2E7 s	Simulation time

A typical workflow with this model to predict the impurities in the cavern would be the following:

1. First, gather all available fixed data, such as cavern size, temperature, pressure ranges, salt content, and sulfate concentrations in the brine.
2. The second step would be probing the brine inside the cavern for microbial activity.
3. If a strong microbial consortium is present in the water phase, growth experiments should be performed to measure pressure, microbial density, gas components over time, and an initial/final sulfate content.
4. The model can be initialized after gathering the microbial data, especially microbial maximum growth rate and gas composition. By matching microbial density, pressure reduction and gas composition, the model is matched.
5. With the matched model, various prediction cases can be run to predict the impurities over the long term.
6. Additional field data for the matching process would be preferable to gain experience on field scale and conclude differences to the laboratory results

The most influential parameter is the mass-transfer coefficient, which defines the components exchange between the phases. This remains an unknown parameter, but the coefficient can be relatively fixed compared to the rest of the parameters.

4. Results

This chapter summarizes the theoretical results of impurity development and provides a short sensitivity analysis of the mass transfer coefficient.

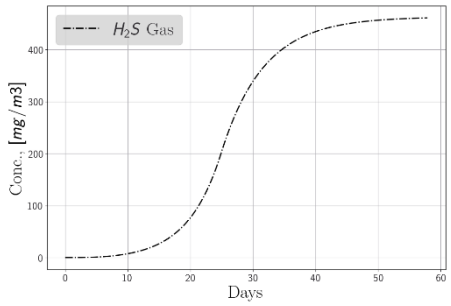

Figure 2 H_2S concentration in the gas phase

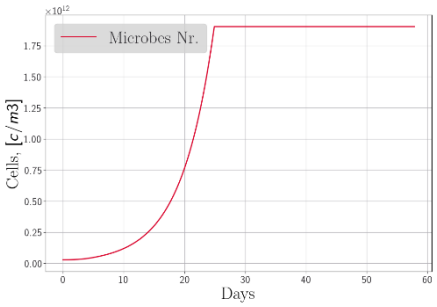

Figure 1 Microbial number in the water phase

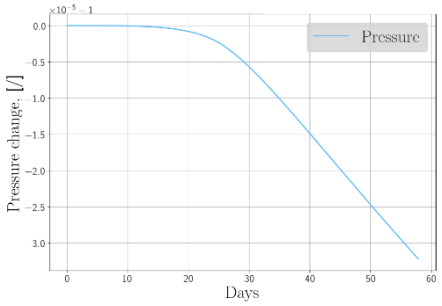

Figure 3 Pressure difference in the gas phase

As can be seen in the three graphs above (Figure 1 – 3), the model simulates reasonable results. The microbial density in the first figure starts rising after the lag phase and reaches a stationary phase due to the completion of one substrate in the water phase. The H_2S concentration in the gas phase increases due to its production in the water phase following its transfer into the gas phase. It also reaches a stationary phase as not much H_2S is produced during the stationary phase of the microbes.
The pressure difference (initial - current) is not strong. The maximum pressure decrease is reached at the end with 3.0E-5. The reduction in pressure can be explained by the dissolvement of hydrogen into the water and only the slow vaporizing of H_2S into the gas stream. The partial pressure shifts; consequently, the H_2 pressure decrease is more substantial than the H_2S pressure rise. In total, this results in a decrease in pressure.

The limiting substrate is not the sulfate in the water; it is the rate at which H_2 dissolves into the water phase, which is dominated by the mass-transfer coefficient. As no active microbes were found in the pilot cavern, the impurification is not as strong as the graphs show. No H2S or other products are expected to be admixed in the gas stream. Other caverns have to be tested individually because the microbial consortium and its activity are the main drivers of impurities. As the results above only show the impact of sulfate-reducer, additional microbes like methanogens can influence the impurity's behavior and the pressure behavior in the cavern.

The pressure's transfer and behavior strongly depend on the mass-transfer coefficient.

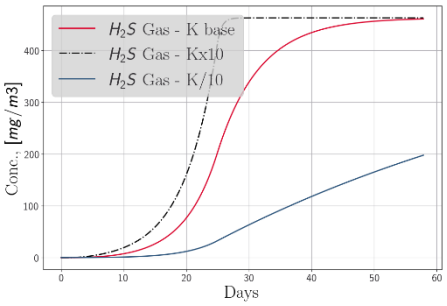

Figure 5: H_2S behavior for different mass transfer

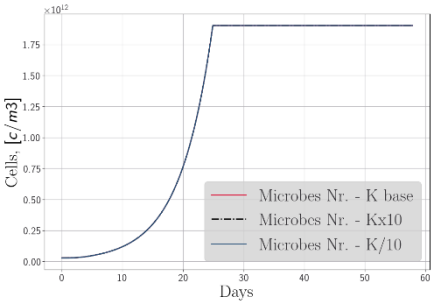

Figure 4: Microbial behavior for different mass transfer

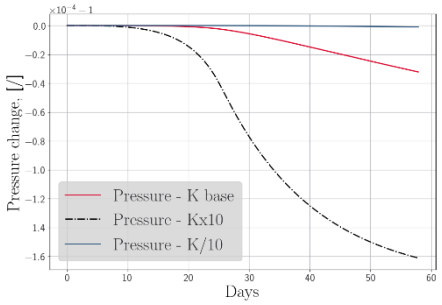

Figure 6: Pressure behavior for different mass transfer

As the sensitivity analysis above shows (Figure 4 – 5), mass transfer mainly impacts the components' solubility and the cavern's pressure behavior. In the base case, the coefficient is set as stated above, and in the two other cases, it is divided and multiplied by factor 10. The parameter does not significantly influence microbial growth. If zoomed in on the 10x case, it gives a slightly higher microbial density. However, due to the lag phase, the microbes' growth is equal to that of the other cases.
The H_2S appearance in the gas phase differentiates between the cases. As the component flux increases (case 10x), the sulfate reduction reaches its plateau earlier, whereas a higher mass flux shows that the concentration in the gas phase is not yet constant. Not all produced H_2S is transferred in the gas phase, even though the microbial growth is stationary.
The pressure behavior compared to the H_2S concentration is comparable. The pressure decrease is more substantial for the higher mass transfer, as more components are transferred and the partial pressure of those components changes. With a low mass transfer (blue line in Figure 6), the pressure reduction is near to unmeasurable.

5. Conclusion

The presented paper shows a theoretical approach to estimating and predicting impurities during hydrogen storage operations in a salt cavern. The approach is a 0-D cavern model with a given size, maximal operating pressure, and temperature. All fixed parameters influence the model. Further, the model couples the mass transfer with a microbial growth model, in this case, the Double Monod model. This allows a non-equilibrium state with an exchange of components between the phases. This exchange is crucial as microbes only live in the water phase.
All in all, the model shows promising results in predicting the behavior of pressure, gas components, and microbial density behavior. The sensitivity analysis also shows the dependency of mass transfer on pressure and component behavior.
The model should be further validated with real operational data at specific in-situ conditions. More growth data, such as a measured growth rate, must be considered to test this model on a field or laboratory scale. For an operator, the model shows that composition monitoring in the gas stream should be considered, and pressure reductions may be not only indicating for leakage but also caused by microbial conversion of hydrogen. These parameters should be measured during operation, particularly in the early period of gas filling the cavern to mitigate potential gas quality changes and associated safety issues during the daily operation.

Acknowledgements

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