POLITECNICO MILANO 1863

SCUOLA DI INGEGNERIA INDUSTRIALE E DELL'INFORMAZIONE

EXECUTIVE SUMMARY OF THE THESIS

Development of an Integrated work-flow for Biochemical Underground Hydrogen Storage Modelling

TESI MAGISTRALE IN ENERGY ENGINEERING – INGEGNERIA ENERGETICA

AUTHOR: ENRICO ANTONELLINI

ADVISOR: STEFANO CAMPANARI, PAOLA PANFILI, GIACOMO RIVOLTA

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1. Introduction

With energy transition happening in the next future years, hydrogen storage solutions for seasonal periods will play a key-role in providing sufficient flexibility to the national energy system together with a correct sizing of renewable energy capacity to be installed thanks to the time-shifting that they can provide to power generation. [1] Lately Underground Hydrogen Storage (UHS) has gain more and more relevance in the scientific community thanks to its high potential storage capacity and lower cost per energy stored if compared to up-surface hydrogen tanks. The four main sub-surface formations that are investigated are: lined rock caverns, salt caverns, deep aquifers, and depleted oil and gas fields. [2] The main focuses of this thesis will be on how to correctly size and operate a real depleted gas field converted into a H_2 storage plant and on the impact of Methanogenic Archaea proliferation in H_2 loss. [3]

2. Field Overview

The real depleted gas field studied in this work is the Nissa field. It can be divided into four levels each one has its own porosity, water saturation and permeability. The level that was simulated in this thesis is the 3rd one (L3): it has an initial water-gas contact at 3225m depth and a static bottom hole pressure (SBHP) equal to 362 bar. This value was considered in the estimation of the maximum BHP at which injector wells could operate, the other physical constrains are reported in Table 1.

External Constrains	
BHP_MAX	360 bar
BHP_min	90 bar
WG-Ratio Max	1.00E-04
Max Flowrate	2% of Capacity

Table 1: Physical constrains for Plant Operation

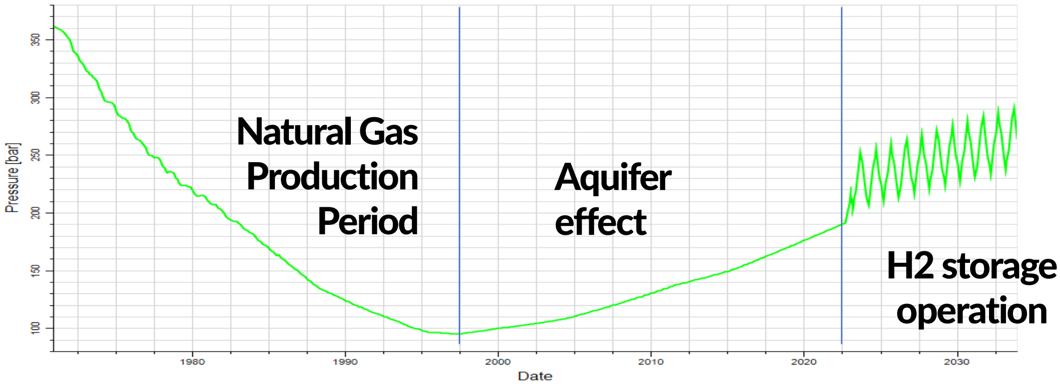


Figure 1: Reservoir pressure evolution during each phase of operation

Figure 1 shows the historic operation of the field that were started in 1970s and ended in 2000s, after that a pressure increase was observed due to the ending of the production phase and the push of the aquifer surrounding the gas saturation region. This particular phenomenon will affect the reservoir behavior when the cycling operations will start and will be further discussed. At last starting from 2020s the response to typical cycle operations of H_2 storage plants is showed.

3. Biological Activity

Between all the different challenges correlated to H_2 storage in porous media one of the more relevant is the proliferation of microorganisms in sub-surface formations. Indeed, microorganisms consume hydrogen for their metabolism causing both hydrogen loss and production of undesired pollutants. The most relevant hydrogenotrophic microorganism are: Methanogenic Archaea, Homo-acetogenic Archaea, Sulphate-reducing Bacteria and Iron-reducing Bacteria. [4]
In literature it was shown that the one that have had the higher impact in H_2 consumption in reservoir-like conditions [5] was the Methanogenic Archaea and is the one that was modelled in this thesis. The reaction incentivized by the Archaea is:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \qquad (3.1)$$

In order to model microorganism proliferation analogies from reported laboratory experiments were done. Particularly Figure 2 shows the microorganism concentration evolution in a batch reactor and six different phases can be distinguished. [6]

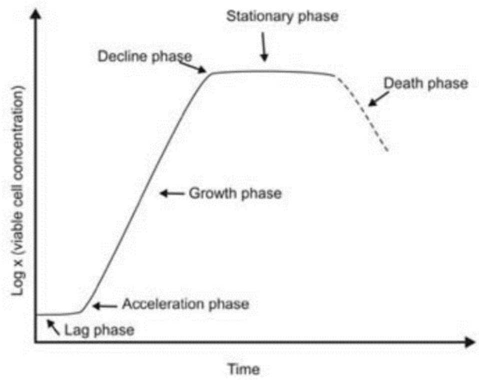


Figure 2: Batch culture microorganism evolution

When the modelling procedure was done not all the phases were included but only the ones directly correlated to proliferation. This choice was motivated by the fact that these species can survive only in aqueous environment and since in the production stream no water is expected their relevance is restricted to their ability to consume hydrogen. Since they will not act as pollutant themselves to model their decay phases would have increase the complexity without bringing any specific improvement to the final results. It is important to point out that any microorganism proliferation happens via duplication of cells and the mechanism can occur only when the cell has already undergone the respiration and nutrition procedures. The respiration process consists in the activation of a RedOx reaction within the microorganism and hydrogen takes the role of electric donor giving the energy necessary to sustain the reaction. Doing that H_2 molecule evolves into different ones (i.e. CH_4 for the

Methanogenic Archaea proliferation). In the meantime the nutrition process is developing: here mass and dimensions of the bacterial cell are increased thanks to the carbon fixation mechanism that require an external organic carbon source, represented by CO_2 for the Methanogenic Archaea case.
One of the most accredited model in the environmental engineering field to represent microorganism proliferation is the Double-Monod model that simply correlates the proliferation rate ψ^{growth} to the aqueous concentration of reactant x^{H_2} and x^{CO_2} through the equation:

$$\psi^{growth} = \psi_{max}^{growth}\left(\frac{x^{H_2}}{\alpha_1+x^{H_2}}\ \frac{x^{CO_2}}{\alpha_2+x^{CO_2}}\right) \quad (3.2)$$

However, Monod-like models and microbial growth in general cannot be simulated in standard commercial reservoir simulator. Then, to analyze the H_2 microbial losses the chemical reaction capabilities of the reservoir simulator software STARS were used. In particular, Archaea proliferation was modelled as a general chemical reaction with a Power-Law to model kinetic. The Power-Law final aspect is reported here:

$$R^{Double-Monod\ approx} = F^{*} c_{H_2}^{\beta_{H2}} \hat{c}_{CO_2}^{\beta_{CO2}} \quad (3.3)$$

With F* (Frequency Factor), β_i (component reaction order) specifically tuned to capture the Double-Monod kinetic in the real reservoir conditions.

4. Methanogens proliferation impact

To evaluate the impact of methanogens on a UHS plant the focus was on a representative sector of the Nissa depleted gas field. The total length of storage operations was restricted to 2 years plus the amount of time dedicated to injecting the cushion gas. Each storage cycle was standardized as a 6 months injection and 6 months production alternation. The original gas in place mole fraction composition was assumed equal to 99% CH_4 and 1% CO_2, while 100% H_2 was used as cushion gas. Sensitivities were then carried out changing cushion gas composition and initial in place CO_2 mole fraction. The losses due to bacterial activity for the base case, presented in Table 2 were evaluated with respect to the same simulation case without activating microorganism proliferation.

	Losses due to Methanogens	H_2 Tot Loss
1° cycle	0.301%	6.36%
2° cycle	0.501%	10.61%
Overall	0.401%	8.49%

Table 2: Base Case Methanogens and Total Losses

It is clear from Table 2 that the losses given by methanogens are very limited with respect to the total amount that includes also H_2 mixing with residual gas in place in the field and H_2 dispersion in the sub-surface porous volume.
Same considerations are true when the cushion gas molecule in use becomes methane as reported in Table 3.

	Losses due to Methanogens	H_2 Tot Loss
1° cycle	0,430%	28,820%
2° cycle	0,590%	22,380%
Overall	0,511%	25,600%

Table 3: CH_4 as cushion Methanogens and Tot Loss

H_2 total losses tend to increase since the cushion gas that should separate hydrogen from the initial gas in place will partially mix with the hydrogen injected itself. This effect is pointed out but unavoidable nonetheless.
The last molecule that was considered as a cushion gas option is CO_2, this configuration could be quite interesting since the same depleted reservoir would act both as H_2 storage and as a CO_2 sequestration system. Unfortunately, the methanogens proliferation makes this solution unfeasible: in fact by looking at Figure 3 it can immediately be seen that the gas production composition is strongly altered by this choice and almost no hydrogen is able to come back to surface without having been transformed into methane.

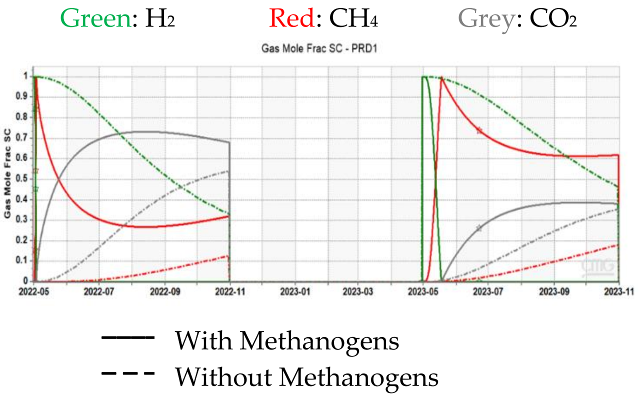


Figure 3: Gas Prod composition for CO_2 as cushion

Given the strong impact of CO_2 presence on the microbial activity the last sensitivity analysis was done on the initial amount present in the reservoir. The Base Case had 1%, a reasonable value for the Nissa field simulated, nonetheless an increase up to 2.5% and 5% was simulated.
Figure 4 shows the findings: the maximum losses were found in the 5% case and the overall value remained always lower than 2.5%.

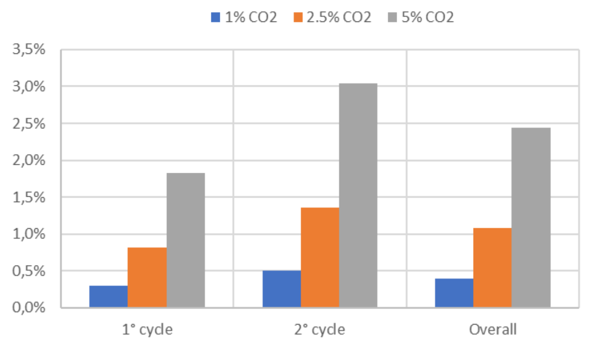


Figure 4: Different H_2 losses depending on Initial amount of CO_2 present in reservoir

It's reasonable to conclude that Methanogenic Archaea proliferate fast so their only limit is the amount of CO_2 they can find in the reservoir since H_2 will always be available given the fact that is the molecule that the plant has to store.

5. Plant Operability as H_2 storage system

Here the focus shifts on realistic UHS scenarios in a depleted gas reservoir, analyzing different operational conditions and evaluating the H_2 storage efficiency. For this purpose, ECHELON reservoir simulator was used instead of STARS. This choice was motivated by the fact that, being a GPU simulator, ECHELON computational performance is considerably better with respect to STARS. Microorganism activity cannot be simulated in ECHELON, however, based on the previous analysis, the impact of microbial H_2 losses can be considered minor and then neglected.
A time-span of ten years was assumed for the simulations and various operational parameters were considered:

- cushion gas amount: which influences initial pressure in the reservoir and marginally gas production purity depending on the molecule chosen
- number of wells in operation: which was useful to understand the real storage capacity of the level analyzed
- schedule flexibility: to better evaluate the plant responds to realistic charge & discharge scenarios based on the energy system outlook in a future decarbonized economy. The data used to realize this schedule were derived from simulations realized in this work [7] and properly tuned for the capacity value of the Nissa field

The Base Case assumed: 1.125E08 Sm^3 H_2 as cushion gas with 5 wells in operation and a 6 months injection 6 months production cyclic alternation. This case presented no physical constrains violation and was used to estimate the overall storage capacity at 633.7 GWh_{LHV}, even though Figure 5 shows that the energy production exceeds this value every year. This is due to the partial mixing happening between H_2 injected and the CH_4 originally in place.

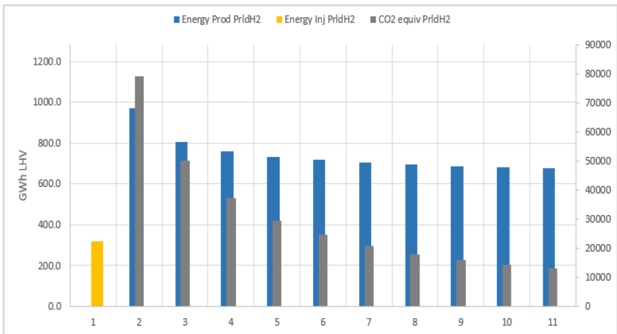


Figure 5: Energy Prod and tCO2 equiv emissions

Given the higher Lower Heating Value [MJ/Sm^3] of methane with respect to hydrogen (33 for methane and 10 for hydrogen) the energy content of the production stream will increase. Moreover, together with methane an equivalent amount of CO_2 emitted (once the methane undergoes a generic combustion process) is given and it's reported in Figure 5 in [tons]. The first sensitivity implemented was to substitute H_2 as cushion gas with CH_4 to evaluate the impact of the mixing with hydrogen that will be reflected in the final amount of energy produced and tCO2 equivalent emitted. Figure 6 gives an insight on what's happening showing that the difference between the two cases is relevant mainly on the first few cycles of operation suggesting that after an initial mixing between H_2 and CH_4 the large density difference between the two will favor the separation between them.

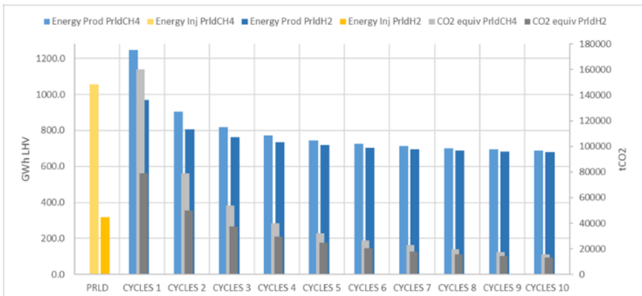


Figure 6: Energy Prod and tCO2 equiv emissions Base Case vs CH_4 as cushion gas

For the next cases H_2 will always be used as cushion gas to maximize the gas production purity. The next parameter that was evaluated is the actual amount of cushion gas to inject which depends strongly on the gas already present in the specific site and the aquifer strength. The Base Case had 1.125E08 Sm^3 so two different alternatives were simulated with half and double the amount.
Injecting half the amount of cushion gas would represent a good economic benefit reducing the upfront costs of the plant. Nevertheless, the sub-surface pressure will oscillate on lower values and this might represent an issue in the production phases as presented in Figure 7 where it can be seen that from the 8^{th} year of operation the gas production rate could not be maintained for the overall 6 months of production due to the reaching of the BHP min limit.

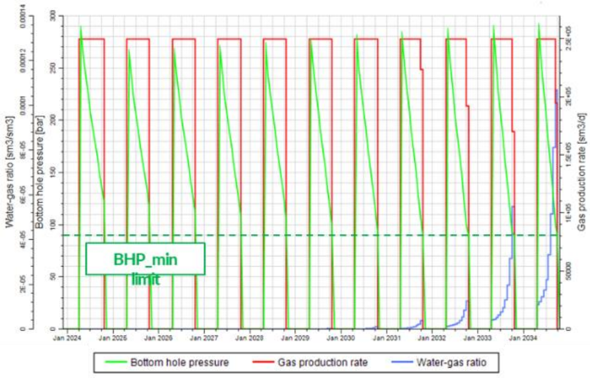


Figure 7: Prod frame with halved cushion gas

The choice to increase the amount of cushion gas injected might seem anti-economic but it might be actually convenient if the lifecycle of the plant is expected to be long and also exceed the decade simulated. In fact as showed in Figure 8, not only no physical limitation is reached but also the water gas ratio is kept much lower with respect to the Base Case suggesting that working at higher reservoir pressure helps to mitigate the aquifer influx.

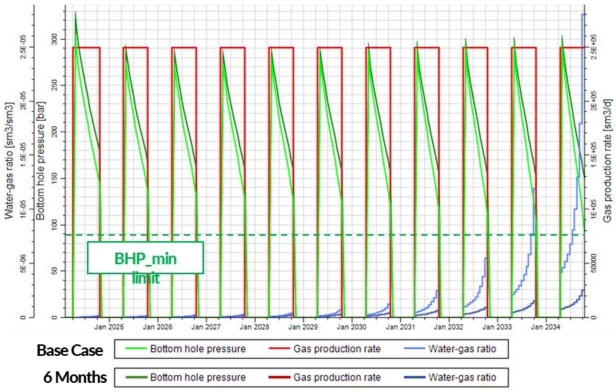


Figure 8: Prod frame with doubled cushion gas

Then the number of wells was varied to understand the actual capacity of the level. With the Base Case having 5 wells, simulations with 7 and 10 wells were carried out keeping constant the total amount of cushion gas injected while the capacity would increase from the initial 633.7 GWh_{LHV} to 887.2 GWh_{LHV} for the 7 wells case and up to 1267.4 GWh_{LHV} for the 10 wells case. These conditions increased the reservoir pressure variations in each cycle, leading to a faster aquifer rise and then higher water gas ratio, reaching the maximum operational limit. Figure 9 shows what happens in the ten wells simulation in which the water – gas ratio limit is reached and the well production is stopped.

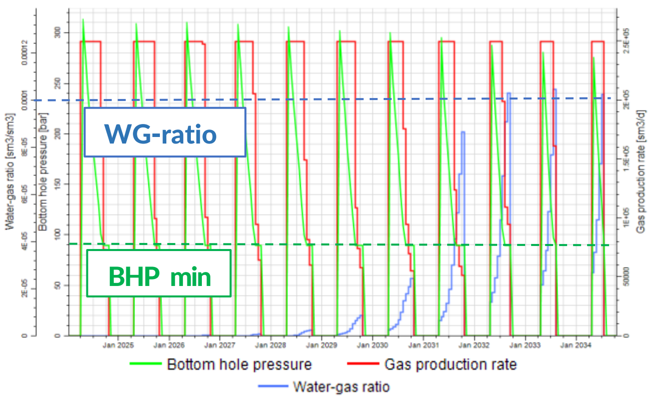


Figure 9: Prod frame with 10 wells in operation

Finally, more realistic cycling schedules were analyzed. Starting from the State of Charge (SoC) graphic presented in Figure 10 and obtained by the data from a study of Politecnico di Milano's energy department. [7] [8]

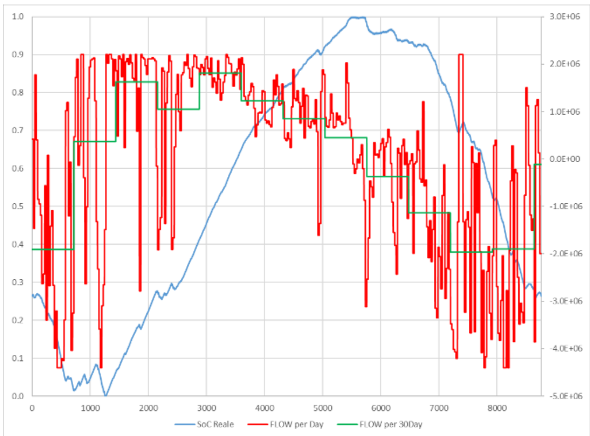


Figure 10: SoC and averaged flowrate

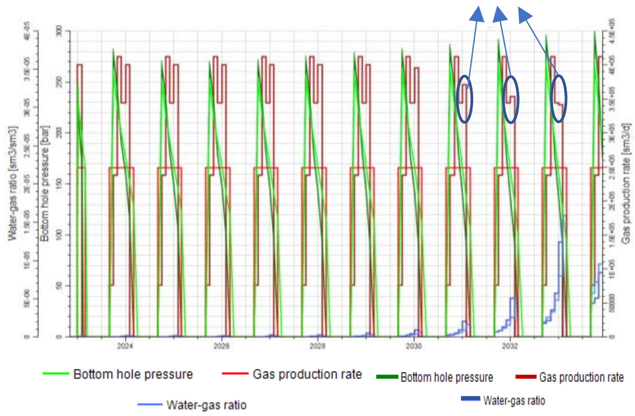
The flowrates of injection and production were evaluated as:

$$Q = \frac{dSoC(t)}{dt} * Q_{tot} \qquad (5.1)$$

with Q: flowrate [Sm³/d] Qtot: Total Capacity [Sm³] The derivative was averaged depending on the scenario that had to be simulated, namely: Monthly Based and Daily Based.

The first analysis on the Monthly Based case gave similar responses to the Base Case, this is mainly due to the seasonal time shift that the facility is undergoing that can be resumed in: 5 months of injection (Feb/yy – Mar/yy – Apr/yy – May/yy – Jun/yy) followed by 7 months of production (Jul/yy – Aug/yy – Sept/yy – Oct/yy – Nov/yy – Dec/yy – Jan/yy+1). Decreasing the time of production per year, actually made this phase more critical as showed in Figure 11; now limitations on the minimum Bottom Hole Pressure are reached even when the capacity value of the facility is kept at 633.7 GWh$_{LHV}$.

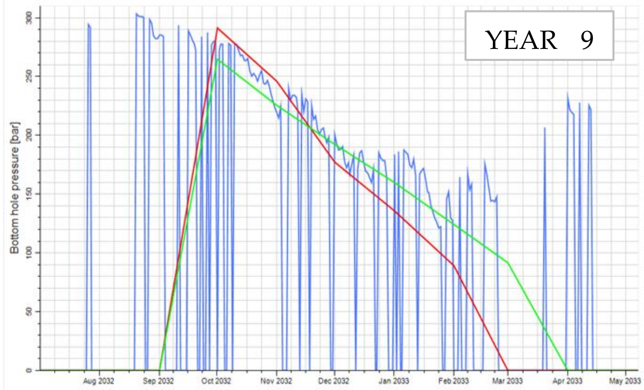
BHP_min limits the Gas Production



Base Case Monthly Based

Figure 11: Gas production framework

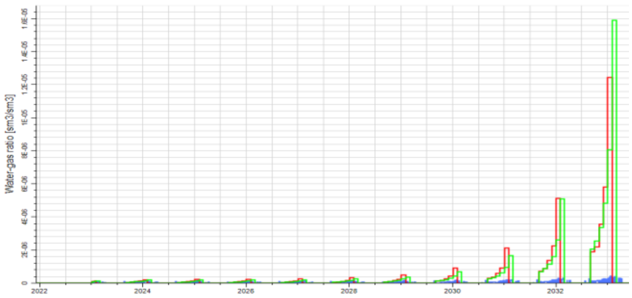
This effect was not present with a Daily Based schedule even if the maximum production flowrate was further increased (always remaining lower than the physical constrain specified). This positive effect first showed the benefit of increasing the flexibility of scheduled flowrate but to actually understand what was happening a representative snapshot of the Bottom Hole Pressure cycling trend was analyzed in Figure 12.



Blue: Daily Red: Monthly Green: 6 Months

Figure 12: BHP evolution during the 9th year

Even if in the Daily variable scenario there are frequent oscillations down to zero (meaning that the well has switched its operation schedule from producer to injector) the values during the production phase are higher on average with respect to the previous case. This helps to not reach the minimum limit and keep the overall reservoir pressure higher. This final effect was testified by Figure 13 that showed the different water-gas ratio increase during the decade of operation and it's clear that a daily flexible scenario would strongly help in managing the aquifer rise.



Blue: Daily Red: Monthly Green: 6 Months

Figure 13: WG ratio evolution during the decade

6. Conclusions

The simulation results on underground microbial activity showed that: Methanogens Proliferation occurs dramatically only when a high amount of CO_2 in reservoir is present (it should be lower than 5% in gaseous phase); this suggests that an evaluation on the initial CO_2 amount present in the facility should be done and that using CO_2 as cushion gas is not an option. Further developments on this area might be:

- The tuning of a Power-Law description for the sulphate-reduction bacteria for realistic storage facilities to evaluate the amount of H_2S that could pollute the gas production stream.
- Since this microbial reactions depends strongly on the SO_4^{2-} and CO_2 present in reservoir a coupling process of the bio-chemical model with the geo-chemical characterization of the reservoir site is required to better evaluate CO_2 presence which is influenced by CO_3^{-} carbonate and SO_4^{2-} evolution that are both strongly correlated to geochemistry

Looking at plant operability simulations the type and amount of cushion gas was defined based on reservoir pressure condition, aquifer control and output stream purity. Then an estimation on the storage capacity of the specific facility was provided together with the storage efficiency. The impact of various charge/discharge schedules was investigated. In the end flexibility benefits were underlined especially regarding equivalent CO_2 emitted throughout 10 years of operation: daily case 258769 tons versus 6 months case 303160 tons. Questions that should be answered in future projects might be:

- well location optimization to minimize aquifer impact
- Evaluation of different flexible schedules based on different SoC evolution
- the operational feasibility related to short charge/discharge cycles

7. References

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